SRI International

6-9129

MULTICLIENT STUDY

CONTRACT REPORT NO. 6 9129-01-SQ

AN ASSESSMENT OF THE CATALYTIC CONVERSION OF NATURAL GAS TO LIQUIDS

Final Report

June 1987

SRI International Project No. 2352

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109pp

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87-05822/

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1 INTRODUCTION

Surging oil prices and the accompanying rapid expansion of worldwide oil and gas drilling activities over the 1973–1985 period resulted in discoveries of an enormous amount of natural gas. Much of the natural gas was found in places that were not near population centers, and the remoteness of those locations often made marketing the gas economically unfeasible.

However, Mobil Corporation developed technology—the methanol-to-gasoline (MTG) process—that can convert natural gas to gasoline, which can be easily transported to a marketing center. Even though the process was relatively expensive, the perception that oil prices were rising served to stimulate interest in the process as a way to use remote natural gas.

The first natural gas to gasoline plant using the Mobil MTG process was commissioned in October 1985, by the New Zealand Synthetic Fuels Corp. The plant is on the west side of North Island and uses offshore natural gas from the Maui Field. The plant is designed to produce 14,450 barrels/day (b/d) of gasoline using two 2,200 ton/day (t/d) methanol plants.

The concept of converting natural gas to gasoline takes advantage of the fact that gasoline prices can be 30%–40% higher than crude oil prices. The large quantities of remote natural gas and the impression that oil prices were in a long-term upward trend provided the economic stimuli for active research in transforming natural gas into high value transportable liquids. The choice of gasoline as a target product was economically sensible—not only because of the relatively high value of gasoline, but also because the large world gasoline market could easily accommodate synthetic gasoline.

SRI has undertaken this study to investigate, analyze, and assess the current research under way to convert natural gas to liquids. This report uses the Mobil MTG process as the base case and then analyzes some new concepts that have the potential to reduce costs considerably. Research is proceeding at a rapid rate in many parts of the world in an effort to discover methods of activating methane. This study presents an impartial assessment of the most promising current processing routes.

SRI International expresses its appreciation to the following clients for their support for this program:

Amoco Corporation
ARCO Chemical Company
British Petroleum Company PLC
Consumers' Gas
E. I. du Pont de Nemours & Company
Elf Aquitaine Norge A/S
Energy, Mines and Resources Canada
ENI (Ente Nazionale Idrocarbure)
Gas Research Institute
Gaz de France
W. R. Grace & Co.
Institut Francais du Petrole
Intevep, S. A.
The M. W. Kellogg Company
Mobil Chemical Company
Ontario Ministry of Energy
Osaka Gas Company Ltd.
Petro-Canada Inc.
Shell Internationale Petroleum Maatschappij B. V.
The U.S. Department of Energy

2 SUMMARY AND PRINCIPAL FINDINGS

Summary

Introduction

This study compares the conceptual process economics of the direct conversion of methane to olefins followed by olefin oligomerization to gasoline (the ARCO route) with the commercially proven route that converts methane to methanol, which is subsequently processed to gasoline (the Mobil route). In addition, we have examined the process economics of transforming methane into mixed alcohols, that are valuable as blending stocks for unleaded gasoline. These and other generalized processing sequences are summarized in Figure 2.1.

Process Descriptions

Mobil's methanol-to-gasoline (MTG) process uses a unique zeolite catalyst, ZSM-5, whose pore structure and catalytic activity produce a relatively narrow range of hydrocarbons in the gasoline boiling range. The finished MTG gasoline has a clear (R+M)/2 octane of about 88 and contains about 28 vol% aromatics. The first commercial plant of its kind began operation in New Zealand in October 1985. The plant can process about 140 million scf/d of natural gas to make synthesis gas that passes through two 2200 t/d methanol trains and 5 fixed-bed MTG reactors to produce about 14,600 barrels per stream day (b/sd) of MTG gasoline. This study has focused on the characteristics of the MTG fixed bed process.

The ARCO Cofeed Catalytic Oxidative Coupling Concept is based on the catalytic reaction of methane and oxygen to form C_2^+ compounds that can be converted to gasoline via oligomerization. The source of oxygen is an air separation plant. This processing route avoids the high capital cost of steam reforming and methanol synthesis, but incurs the capital cost of air separation. The oxidative coupling reactions produce a hydrocarbon mixture that contains a large proportion of ethylene and propylene. For this evaluation, we have assumed a multibed reactor with intercooling and staged oxygen feed. The yield and conversion relationship is based on the use of the manganese-sodium pyrophosphate on silica catalyst. The oxidative coupling product mixture is then converted to gasoline by an oligomerization process. ARCO indicates that an ethylene-rich olefinic material can be converted to liquid hydrocarbons in the gasoline boiling range in the presence of ZSM-5 zeolites and crystalline borosilicate molecular sieve catalysts. We have assumed that this operation is technically achievable because ethylene is proposed as an intermediate in the catalysis of methanol to gasoline.

The ARCO Redox Catalytic Oxidative Coupling Concept (the Redox system) differs from the cofeed system in that the reaction system uses a fluidized bed of oxidized catalyst. The catalyst is the oxygen carrier and donor. As it is in fluidized catalytic cracking (FCC) in normal refinery operations, the catalyst is regenerated by oxidation with air in a zone that is separate from that for methane conversion. The Redox system requires a more complex reactor design than does the Cofeed system, but no air separation system is needed to provide oxygen.

However, the Redox reaction and regeneration system is estimated to cost considerably more than a conventional gas oil FCC unit. The Redox reactor operates at about 1500°F, whereas an FCC unit proceeds at about 1000°F. Regenerator temperature is about 1500°F for the Redox system, compared with 1250°F for an FCC unit. The Redox system requires oxygen to oxidize the catalyst, which in turn, provides oxygen as a reactant in the oxidative coupling reactor. Many times more air is required in the regenerator than in a conventional FCC unit, which burns only carbon off the catalyst. Our cost estimates indicate that the presumed advantage of using air instead of oxygen is completely offset by the greater capital required for the more complex Redox reaction system.

The products from the oxidative coupling reactor are assumed to be the same as those obtained from the Cofeed system. These reaction products are then oligomerized to gasoline.

SRI's choice of design conditions for the Redox reactor based on the selectivity versus conversion data for the manganese–sodium pyrophosphate on silica catalyst, resulted from ARCO's advice to use a methane conversion of about 25% per pass and a selectivity to C_2^+ products of about 75%. Our estimates for each ARCO concept are based on those conditions. We did not attempt to determine the economically optimal selectivity versus conversion condition in detail. However, Table 2.1 and Figure 2.2 provide data on a hypothetical optimization. (Tables and figures throughout the report appear at the end of each chapter in which they are cited.)

The estimates in Table 2.1 illustrate how changes in selectivity and conversion can minimize the capital cost per unit of product.

The mixed Alcohols from Natural Gas via the Dow/Union Carbide SYGMAL Process concept is based on the conversion of natural gas to synthesis gas and subsequent reaction to a mixture of alcohols. The mixed alcohols can be used as a high octane blending stock for unleaded gasoline. In this study we have used natural gas steam reforming for syngas generation. The synthesis gas is then reacted in the presence of a modified Fischer–Tropsch molybdenum–based catalyst to yield a range of alcohols having a 30:70 weight ratio of methanol to higher alcohols (C_2–C_5). The final mixed alcohols product contains 0.1 wt% of water. The blending octane number of the mixed alcohols varies with the composition of the unleaded gasoline base stock and to a lesser extent with the methanol to higher alcohols ratio. The mixed alcohols blending octane number, (R+M)/2, generally falls in the range of 100–120. The addition of 5–10% of mixed alcohols to gasoline causes about a 2–psi increase in the Reid vapor pressure.

Summary of Process Costs

Capital costs for the four processes studied are summarized in Table 2.2.

We have assumed that annual capital charges would amount to 20% of the total fixed capital. These charges are composed mainly of return on investment, interest, and taxes. Depreciation is not included in the capital charges. The cost of production for each of the four processes studied, assuming a natural gas cost at the plant gate of \$0.50/10^9 Btu, is summarized in Table 2.3. The cost of production of the three gasoline–producing processes are essentially the same (within the accuracy of the estimates), regardless of the route from natural gas. Mixed alcohols are considerably less expensive than the gasoline processes because no step is required to convert alcohols to gasoline. However, the market for mixed alcohol

blending is in an early stage of development and its potential is only a fraction of that of the gasoline market. Nevertheless, potential for constructing many mixed alcohol plants exists.

Because the main motivation behind these processes is to use remote natural gas, it is also logical to inquire about the cost of the processes that convert natural gas to liquid products that compete with fuel oil. Although that aspect of the general subject of using remote natural gas was beyond the scope of this study, we have provided a comprehensive summary based on previous SRI analyses. Thus, the comparison of the costs for converting methane to transportable liquids, which are summarized in Table 2.4, is divided into fuel oil competitive processes and gasoline competitive processes. Four products are used to demonstrate the fuel oil competitive picture: (1) methanol fuel; (2) liquefied natural gas; (3) Fischer-Tropsch liquid; and (4) mixed alcohols.

The Value of Natural Gas

For all of the processes that use natural gas, the value of gas at the plant gate is crucial. By assuming a crude oil price, and therefore an accompanying gasoline and a low sulfur fuel oil price, the value of natural gas at the plant gate can be calculated for each process application. To demonstrate this technique, we have assumed that crude oil prices will rise to $44/b (1986 dollars) by 2020, as shown in Table 2.5. We have also assumed that the price of unleaded gasoline will be about 38% greater than that for crude oil and that the price for low sulfur fuel oil will be about 88% of the crude oil price. The calculations in Table 2.5 assume a U.S. Gulf Coast location. Adjustments for specific plant locations and specific competitive marketing areas will alter these estimates. However, the principles will remain the same.

When the negative values for natural gas are shown in Table 2.5 and Figure 2.3, they indicate that the particular processing operation for using natural gas is not economically attractive in world market competition. However, decisions to build and operate a facility may also be based on other factors such as providing employment, currency strategies, and political concerns.

Natural gas values generally become positive when crude oil price exceeds $30/b (1986 dollars), which is projected to occur after the year 2000. The general relationship between natural gas value and crude oil price is shown in Figure 2.4. The use of mixed alcohols for octane blending in unleaded gasoline will give positive values for natural gas when the crude oil price is higher than $20/b (1986 dollars).

Principal Findings

1. The Mobil MTG fixed bed process for converting natural gas will produce gasoline at about $47/b ($1.11/gal) at zero value for natural gas, using U.S. Gulf Coast construction costs for 1986. For a natural gas value of $1.00/$10^6$ Btu, the cost of gasoline increases by slightly more than $10/b ($0.24/gal). These costs are probably the maximum because Mobil is improving the process. However, insufficient data have been published to quantify such process improvements. The processing route via methanol is likely to retain the relatively high capital costs for steam reforming and methanol synthesis.

2. The ARCO concept of catalytic oxidative coupling of methane to produce C_2^+ olefins is not selective enough in the optimum conversion range to provide a distinct economic advantage over the syngas based route used by Mobil. Because the products of the reaction are more easily activated than methane, the greatest selectivity occurs under conditions that give the lowest conversion. Even though syngas and oxidative coupling reactions are effected at high temperatures, the syngas reactions are endothermic and readily carried out in a furnace. The oxidative coupling reactions are highly exothermic, and therefore they require more costly equipment. The ARCO Redox concept uses a fluidized bed operating at temperatures considerably higher than a refinery FCC unit. Such a reactor will require tests in a relatively large pilot plant to demonstrate the feasibility of operation.

3. The ARCO technique for the catalytic oxidative coupling of methane produces ethylene as the major product. Process studies should be made to determine the technical and economic feasibility of recovering ethylene, steam cracking other hydrocarbons to ethylene, and converting ethylene to linear low-density polyethylene (LLDPE). The world LLDPE market is relatively large and is growing at a reasonable pace. The price of ethylene is related to crude oil price in Figures 2.5 and 2.6.

4. The OPEC price war of 1986 and the collapse of oil prices considerably reduced the current economic incentive for converting remote natural gas to gasoline. The world contains a huge and growing amount of natural gas that cannot be economically exploited at present. However, the long-term outlook is still for a steady upward trend in oil prices, provided world economic growth continues at a rate sufficient to reduce world unemployment and provided OPEC continues to moderate competition among its members.

Table 2.1

HYPOTHETICAL OPTIMIZATION OF CONVERSION AND SELECTIVITY FOR ARCO CATALYTIC OXIDATIVE COUPLING OF METHANE

Conversion per Pass (percent of total feed methane)	C_2^+ Selectivity (mol% of fresh feed)	Capital Cost Index $(1 + \text{Recycle Ratio})^{0.5}$	Capital Cost Index Per Unit of Product
5	97	224	2.31
10	92	158	1.72
15	87	129	1.48
20	82	112	1.37
25	75	100	1.33
30	66	91	1.38
35	56	85	1.52
40	46	79	1.72

Table 2.2

SUMMARY OF CAPITAL COSTS

(Millions of 1986 Dollars*; U.S. Gulf Coast)

	Mobil MTG	ARCO Cofeed	ARCO Redox	Dow/UCC Mixed Alcohols
Capital cost				
Steam reforming	94	—	—	104
Methanol synthesis	76	—	—	—
Alcohols synthesis	—	—	—	177
Methanol to gasoline	106	—	—	—
Air separation	—	95	—	—
Oxidative coupling	—	83	173	—
Oligomerization	—	113	113	—
Battery limits	276	291	286	281
Off-sites	145	154	151	176
Total fixed capital	$421	$445	$437	$457
Gasoline production, b/sd	7,640	8,060	8,060	16,600
Total fixed capital, $/b/sd	55,100	55,200	54,200	27,500
Thermal efficiency, %†	50.2	45.5	45.6	60.2
Input natural gas, 10^9 scf/d	77.2	89.8	89.7	95.3
Total fixed capital, $/mcf/d	5.45	4.96	4.87	4.80

*All dollar values in this report are given in U.S. dollars.

†Product heat content, percent of total natural gas heat content.

Table 2.3

SUMMARY OF COST OF PRODUCTION
(1986 Dollars per Barrel of Product; U.S. Gulf Coast)

	Mobil MTG	ARCO Cofeed	ARCO Redox	Dow/UCC Mixed Alcohols
Capital charges	$33.56	$33.63	$33.02	$16.75
Operating and maintenance	13.12	10.70	10.72	6.23
Natural gas	5.16	5.69	5.68	2.89
Cost of production (fob)	$51.84	$50.02	$49.42	$25.87
Dollars per gallon	1.23	1.19	1.18	0.62

Table 2.4

COMPARISON OF COSTS OF PROCESSES TO CONVERT METHANE TO TRANSPORTABLE LIQUIDS

1984 DOLLARS
US GULF COAST LOCATION
PEP COST INDEX = 445
ON STREAM TIME = 90 %
SHIPPING DISTANCE = 6000 NM

FUEL OIL COMPETITIVE PROCESSES (C/MM BTU)	METHANOL FUEL			LIQUEFIED NATURAL GAS			FISCHER-TROPSCH LIQUID			DOW/UCC MIXED ALCOHOLS		
NATURAL GAS PRICE, C/MM BTU	0	50	100	0	50	100	0	50	100	0	50	100
PROCESS COSTS												
CAPITAL CHARGES	272	272	272	126	126	126	445	445	445	476	476	476
OPER & MAINTENANCE	53	53	53	92	92	92	197	197	197	177	177	177
NATURAL GAS	0	74	149	0	61	122	0	132	263	0	82	164
TOTAL (FOB)	325	399	474	218	279	340	642	774	905	653	735	817
SHIPPING	84	84	84	140	140	140	38	38	38	57	57	57
REGASIFICATION & PIPELINING				56	56	56						
TOTAL (CIF)	409	483	558	414	475	536	680	812	943	710	792	874
	@ 2.70 MM BTU/B						@ 5.38 MM BTU/B			@ 3.52 MM BTU/B		
TOTAL AG IS(CIF), $/B	11.35	13.41	15.48				36.56	43.63	50.70	24.99	27.87	30.76
TOTAL AG IS(CIF), C/GAL	27	32	37				87	104	121	60	66	73
	@ 6.00 MM BTU/B			@ 6.00 MM BTU/B			@ 6.00 MM BTU/B			@ 6.00 MM BTU/B		
TOTAL (CIF), $/B FOE	24.54	29.00	33.46	24.84	28.50	32.16	40.80	48.69	56.59	42.60	47.51	52.43

GASOLINE COMPETITIVE PROCESSES, $/B	MOBIL MTG			ARCO COFEED			ARCO REDOX			DOW/UCC MIXED ALCOHOLS		
NATURAL GAS PRICE, C/MM BTU	0	50	100	0	50	100	0	50	100	0	50	100
PROCESS COSTS												
CAPITAL CHARGES	33.56	33.56	33.56	33.63	33.63	33.63	33.02	33.02	33.02	16.75	16.75	16.75
OPER & MAINTENANCE	13.12	13.12	13.12	10.70	10.70	10.70	10.72	10.72	10.72	6.23	6.23	6.23
NATURAL GAS	0.00	5.16	10.31	0.00	5.69	11.37	0.00	5.68	11.36	0.00	2.89	5.77
TOTAL (FOB)	46.68	51.84	56.99	44.33	50.02	55.70	43.74	49.42	55.10	22.98	25.87	28.75
SHIPPING	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
DRYING										1.00	1.00	1.00
TOTAL (CIF)	48.68	53.84	58.99	46.33	52.02	57.70	45.74	51.42	57.10	25.98	28.87	31.75
TOTAL (CIF), C/GAL	116	128	140	110	124	137	109	122	136	62	69	76

SOURCE: SRI INTERNATIONAL

Table 2.5

ECONOMIC COMPARISON OF PROCESSES TO CONVERT METHANE TO TRANSPORTABLE LIQUIDS

1986 DOLLARS
US GULF COAST LOCATION
PEP COST INDEX = 445
ON STREAM TIME = 90 %
SHIPPING DISTANCE = 6000 NM

	1986	1990	1995	2000	2005	2010	2015	2020
ASSUMED OIL PRICES								
CRUDE OIL, $/B	15	21	28	28	28	32	38	44
GASOLINE, $/B	21	29	39	39	39	44	52	61
RESID FUEL OIL, $/B	13	18	25	25	25	28	33	39
RESID FUEL OIL, C/MM BTU	220	308	411	411	411	469	557	645
	VALUE OF NATURAL GAS AT PLANT GATE (C/MM BTU)							
FUEL OIL COMPETITIVE								
METHANOL FUEL	-127	-68	1	1	1	41	100	159
LIQUEFIED NATURAL GAS	-159	-87	-3	-3	-3	45	118	190
FISCHER-TROPSCH LIQUID	-175	-141	-102	-102	-102	-80	-47	-13
DOW/UCC MIXED ALCOHOLS	-295	-242	-180	-180	-180	-145	-92	-39
GASOLINE COMPETITIVE								
MOBIL MTG *	-271	-191	-97	-60	-60	-1	87	176
ARCO COFEED *	-225	-153	-68	-34	-34	20	100	180
ARCO REDOX *	-220	-148	-63	-28	-28	25	105	185
DOW/UCC MIXED ALCOHOLS	-92	52	219	219	219	315	459	602

* ASSUMES A 10% REDUCTION IN CAPITAL COST AND A 10% IMPROVEMENT IN YIELD BY THE YEAR 2000

SOURCE: SRI INTERNATIONAL

Figure 2.1

METHANE TO LIQUIDS PROCESSING ROUTES

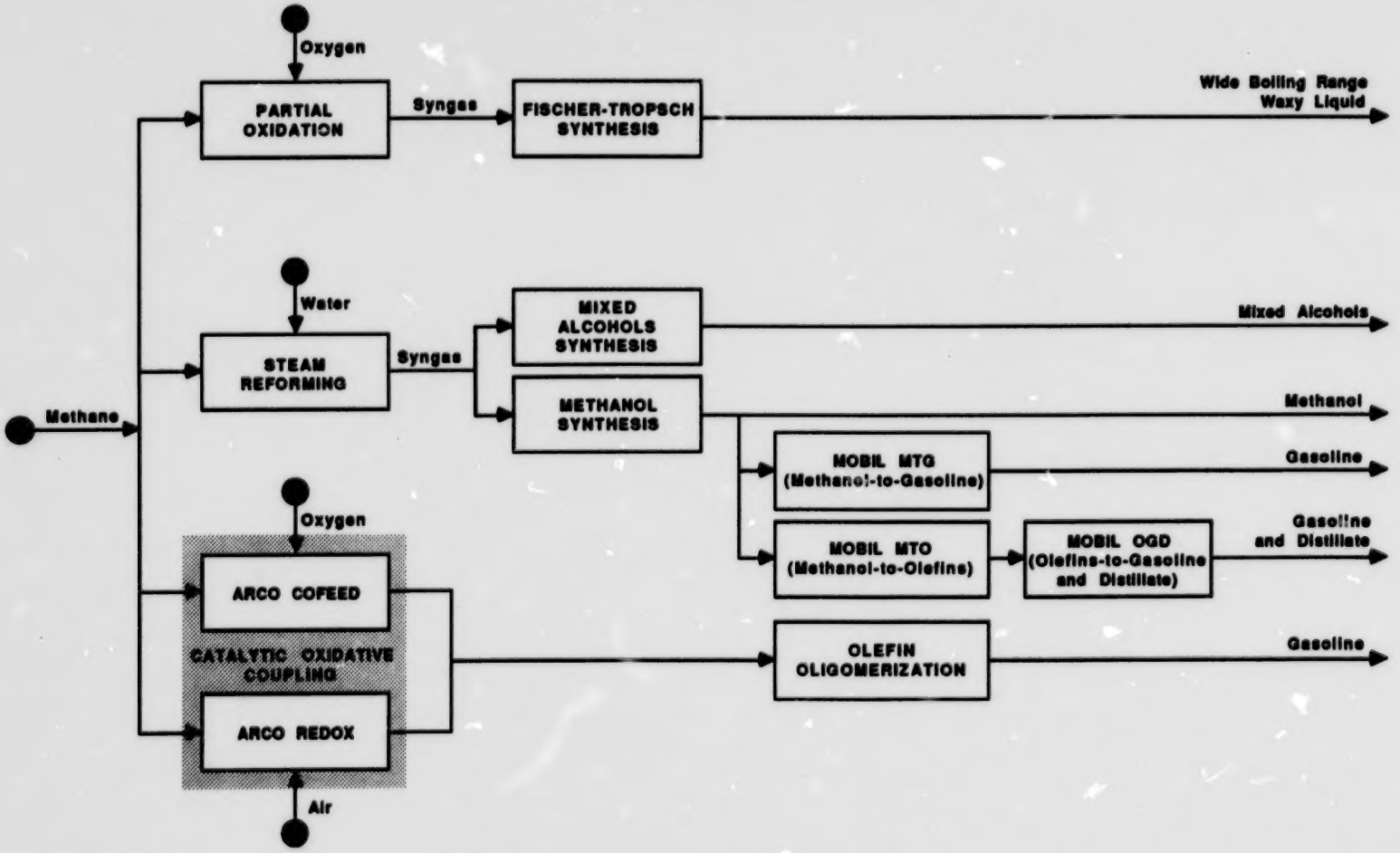


Figure 2.2

HYPOTHETICAL OPTIMIZATION OF CONVERSION AND SELECTIVITY FOR ARCO CATALYTIC OXIDATIVE COUPLING OF METHANE

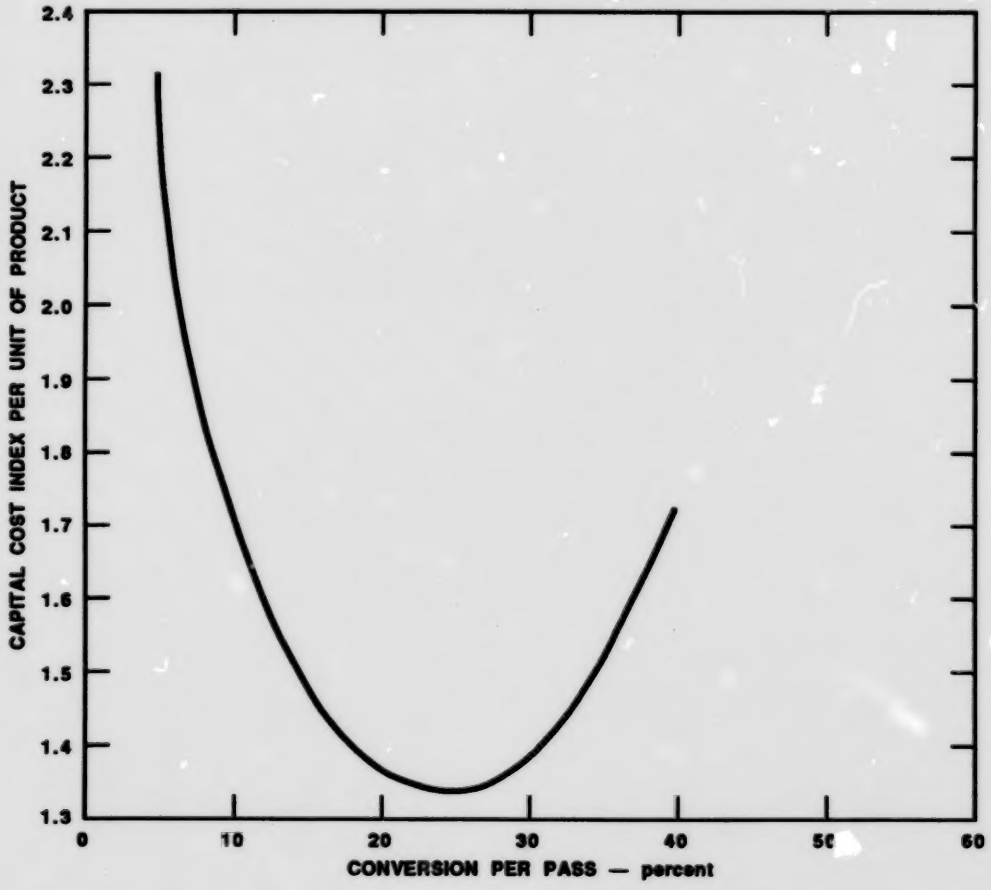


Figure 2.3
VALUE OF NATURAL GAS FOR VARIOUS PROCESSES THAT CONVERT NATURAL GAS TO TRANSPORTABLE LIQUIDS, 1986-2020

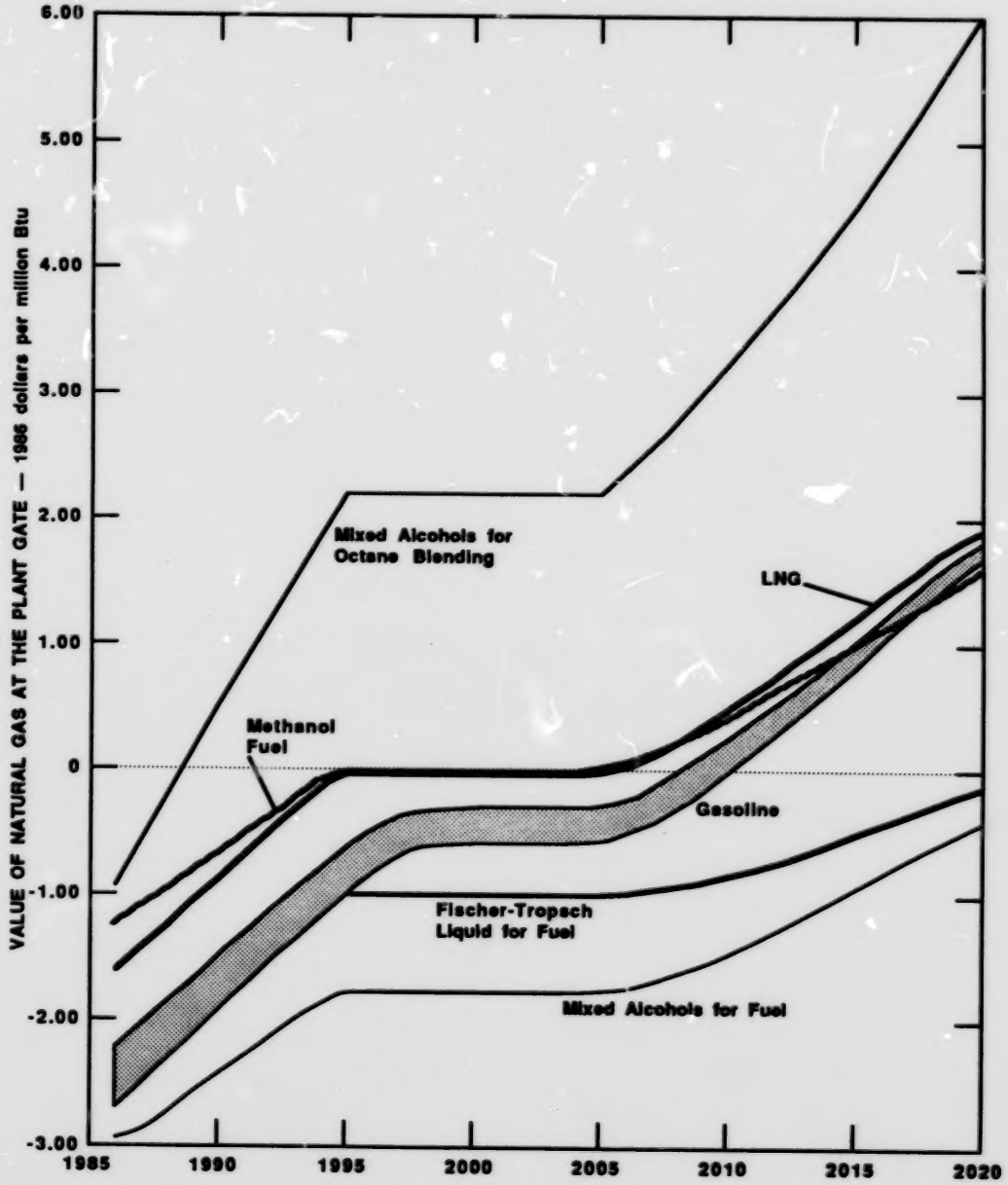


Figure 2.4

VALUE OF NATURAL GAS AS A FUNCTION OF CRUDE OIL PRICE FOR PROCESSES THAT CONVERT NATURAL GAS TO TRANSPORTABLE LIQUIDS

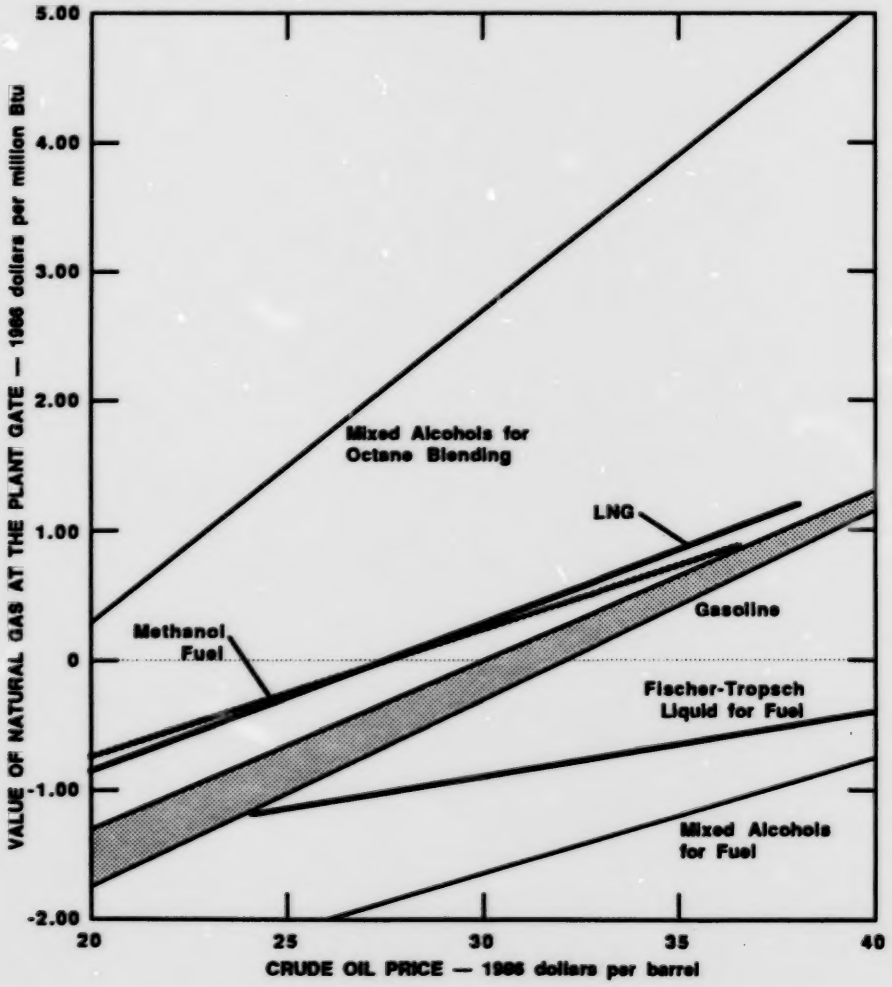


Figure 2.5

CRUDE OIL AND ETHYLENE SPOT PRICES, 1972-1986

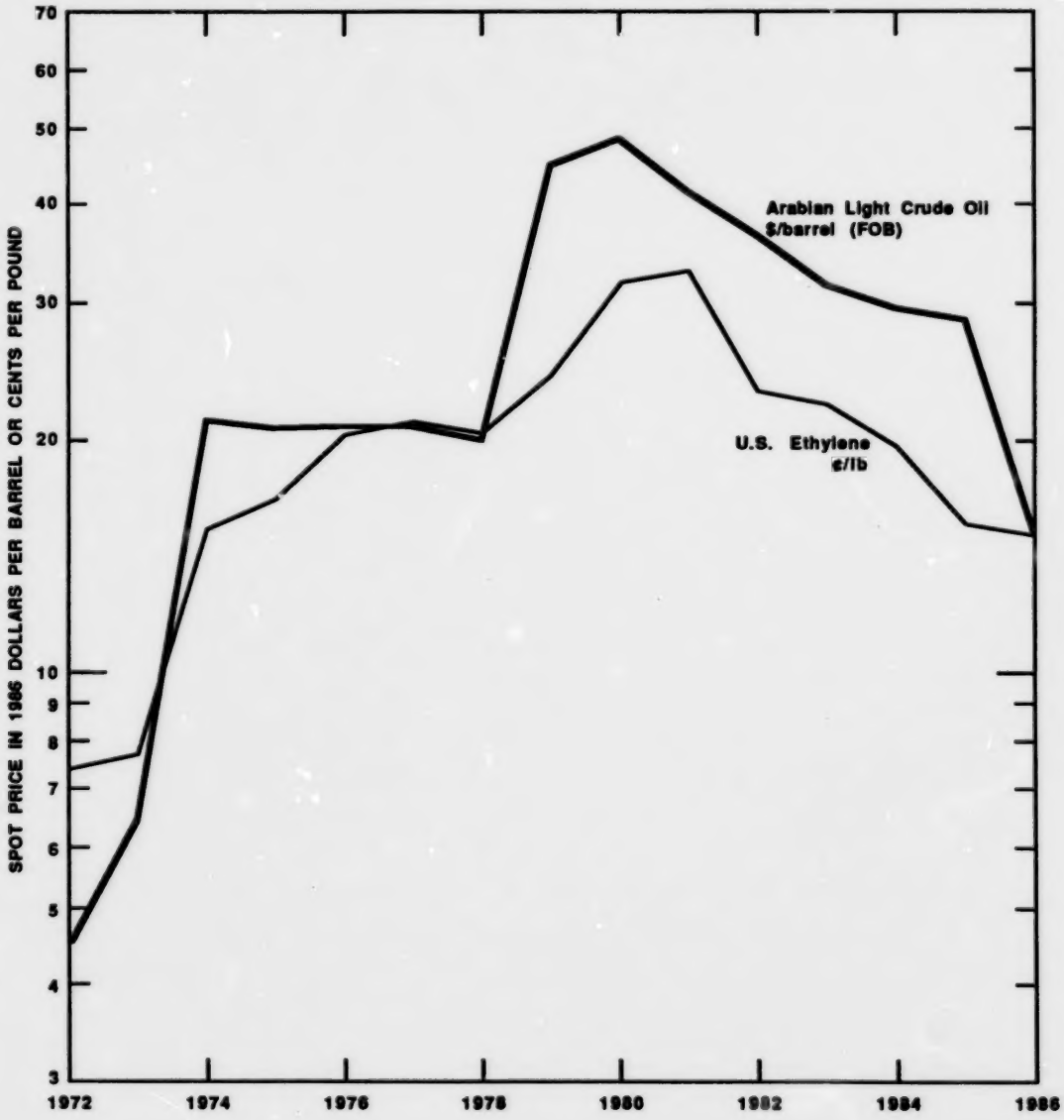
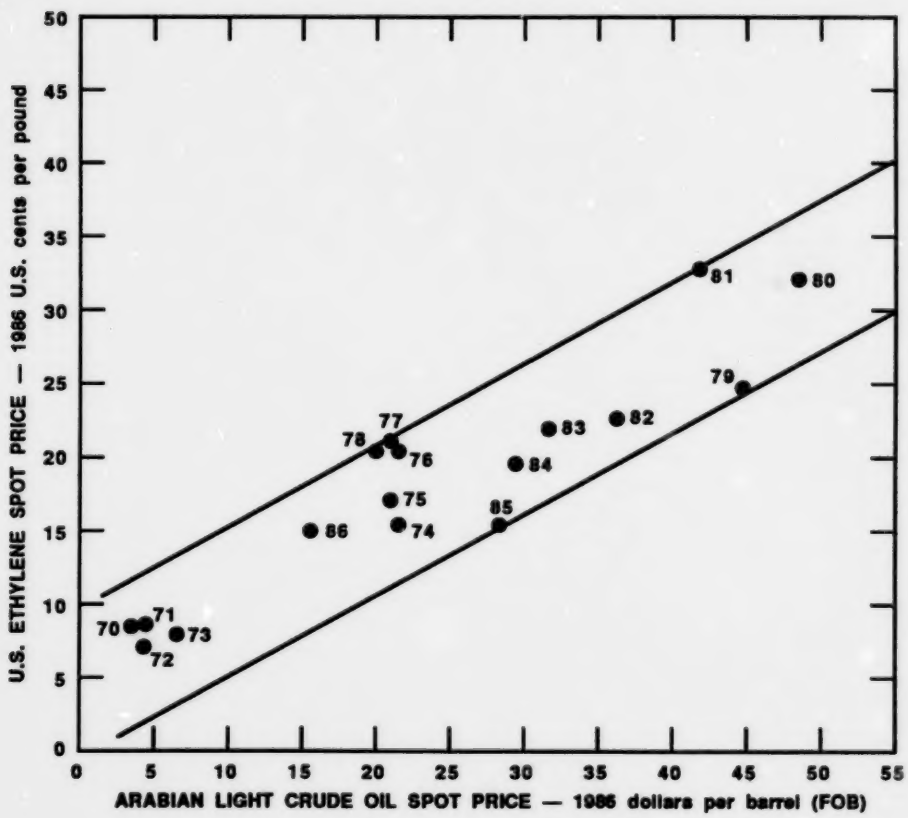


Figure 2.6

U.S. ETHYLENE PRICE AS A FUNCTION OF
ARABIAN LIGHT CRUDE OIL PRICE, 1970-1986



3 WORLD NATURAL GAS AVAILABILITY

The soaring oil prices of the 1970s and 1980s provided the confidence and incentive for a rapid expansion of worldwide oil and gas drilling activities. From 1970 through 1985, world natural gas reserves grew at an average rate of 5.4%/y. Gas reserves rose from 1587 trillion (10^{12}) cubic feet (tcf) in 1970 to 3484 tcf in 1985, as shown in Tables 3.1 and 3.2 and Figure 3.1. One way to comprehend the magnitude of these quantities of natural gas is to put them in terms of a barrels of crude oil equivalent, as shown in Table 3.3, and then compare the natural gas reserves with crude oil reserves, as shown in Figure 3.2 and below:

WORLD NATURAL GAS AND CRUDE OIL RESERVES
[Billions (10^9) Barrels]

	1970	1975	1980	1985
Crude oil	611	659	649	700
Natural gas	271	382	451	596

These tables and figures clearly indicate the rapidly growing importance of natural gas a world energy resource. An extrapolation of past trends indicates that the reserves of natural gas will surpass those of crude oil in the 1990s.

The marketed production of world natural gas has risen at an average rate of 3.9%/y, from 38.1 tcf/y in 1970 to 67.8 tcf/y in1985, as shown in Table 3.4 and Figure 3.3. Reserves grew faster than marketed production, with the reserves:production ratio for world natural gas rising from 42 years in 1970 to 51 years by 1985, as shown in Table 3.5. Over the same time period, the ratio of world crude oil reserves to production was essentially constant at 36 years. These figures indicate the world has ample reserves of oil and natural gas. Most of the problems associated with the use of these energy resources are related to their national and geographic distribution.

It is useful to compare oil and gas production in common units to gain a perspective on trends since 1970, as shown in Figure 3.4 and below:

WORLD CONSUMPTION OF OIL AND NATURAL GAS, 1970–1985
(Millions of Barrels per Day)

	1970	1975	1980	1985
Crude oil	45.2	53.6	59.3	53.2
Natural gas	17.8	22.1	27.6	31.8
Total	63.0	75.7	86.9	85.0

The figures for the 1970–1985 period indicate average growth rates of 1.1%/y for crude oil and 3.9%/y for natural gas. The rapid increase in natural gas use has served as an important force in moderating oil prices.

Much of the natural gas has been found in places remote from population centers. To make use of that gas, the primary option is to build an overland pipeline to tie into an existing infrastructure. The most prominent recent example of exercising that option was the installation of a natural gas pipeline from the Soviet Union to Western Europe. It allowed the USSR to obtain hard currency from its natural gas reserves, which soared from 426 tcf in 1970 to 1550 tcf in 1986.

However, a great deal of natural gas exists in areas that are too remote to be economically transported. A portion of that natural gas is associated with crude oil production. In the past, associated natural gas was flared and thus wasted. However, the trend has shifted to reinjection of the natural gas to help maintain oil reservoir pressure and to conserve the gas.

Remote natural gas exists in such areas as the Alaskan North Slope, the Canadian Arctic islands, the Tierra del Fuego region of South America, Western Australia, the North Sea, and numerous offshore locations. The huge amounts of gas and the need to obtain value for that gas are providing the driving forces for the worldwide research activities related to converting natural gas to liquids. Current research is aimed at the production of synthetic gasoline primarily because of the large world gasoline market, which is shown below:

FREE WORLD GASOLINE DEMAND
(Millions of Barrels per Day)

	1980	1985
United States	6.6	6.8
Western Europe	2.5	2.6
Japan	0.6	0.6
Canada	0.7	0.6
All others	2.4	2.5
Total	12.8	13.1

A single train natural gas to gasoline plant would use about 80 million scf/d of natural gas to make about 8,000 b/d of gasoline. Thus, a large number of synthetic gasoline plants could easily be accommodated in the world gasoline market.

Table 3.1

WORLD NATURAL GAS RESERVES
(Trillions [10^{12}] of cubic feet)

	1970	1975	1980	1985
WESTERN HEMISPHERE				
UNITED STATES	265.0	215.0	191.0	197.0
CANADA	60.5	53.4	87.3	99.7
LATIN AMERICA	73.1	90.5	159.8	189.3
SUBTOTAL	398.6	358.9	438.1	486.0
WESTERN EUROPE	147.7	180.9	159.3	226.4
AFRICA	191.5	207.1	208.5	198.4
ASIA-PACIFIC	56.3	111.6	126.3	171.5
MIDDLE EAST	354.2	538.8	752.4	855.8
TOTAL FREE WORLD	1148.3	1397.3	1684.6	1938.1
COMMUNIST COUNTRIES	438.5	835.0	953.9	1546.0
TOTAL WHOLE WORLD	1586.8	2232.3	2638.5	3484.1

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* INCLUDES 1/2 NEUTRAL ZONE

SOURCE: SRI INTERNATIONAL

Table 3.2

HISTORICAL WORLD NATURAL GAS RESERVES (AT YEAR-END)

(Trillions [10^{12}] of cubic feet)

	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986
NON-OPEC																	
WESTERN HEMISPHERE																	
UNITED STATES	265.0	269.6	271.5	267.3	258.0	215.0	229.0	210.0	205.0	194.0	191.0	198.0	204.0	198.3	198.0	197.0	185.4
CANADA	60.5	56.4	55.0	50.3	52.5	53.4	56.0	58.0	59.0	65.5	87.3	89.9	97.0	90.5	92.3	99.7	99.6
MEXICO	10.0	11.5	11.5	11.0	15.0	12.0	12.0	30.0	32.0	59.0	64.5	75.4	75.9	75.4	77.0	77.0	76.5
ARGENTINA	8.0	7.6	8.0	8.0	7.5	7.2	6.0	6.1	12.0	15.2	22.0	23.4	25.2	24.4	24.6	22.6	23.0
TRINIDAD/TOBAGO	3.5	5.0	7.5	5.0	6.0	4.0	3.4	8.5	8.0	8.0	12.0	10.8	11.0	13.1	10.6	10.5	10.0
OTHER WEST HEMISPH	18.0	17.2	16.3	20.3	23.7	20.3	15.0	16.0	16.0	15.5	15.3	15.4	16.3	15.5	14.3	15.0	17.1
SUBTOTAL	366.6	365.3	370.6	361.9	354.7	311.9	313.6	338.6	332.0	377.2	392.1	412.9	429.4	416.9	416.8	422.8	412.0
WESTERN EUROPE																	
NORWAY	3.0	10.0	15.0	23.0	24.7	25.0	18.5	20.0	24.0	23.5	42.7	49.4	58.0	58.8	89.0	108.0	103.2
NETHERLANDS	83.0	83.0	88.0	92.0	94.8	70.0	61.9	60.0	62.0	59.5	62.0	55.7	51.9	50.1	48.5	47.1	70.4
UNITED KINGDOM	36.0	40.0	45.0	50.0	50.0	50.0	30.0	29.0	27.0	25.0	24.0	26.0	25.4	25.1	27.0	33.0	33.4
WEST GERMANY	11.9	14.0	12.7	12.3	11.5	8.3	7.5	7.3	6.3	6.4	6.0	6.2	6.3	6.8	6.0	6.4	6.5
OTHER WEST EUROPE	13.8	16.3	17.7	16.5	21.8	27.6	24.0	21.9	24.0	21.0	23.8	13.4	15.1	16.5	15.4	15.9	16.2
SUBTOTAL	147.7	163.3	178.4	193.8	202.8	180.9	141.9	138.2	143.3	135.4	159.3	150.7	156.7	157.3	206.7	226.4	229.7
AFRICA	7.5	10.5	9.5	8.2	7.4	8.0	10.9	11.3	12.7	13.4	11.7	16.5	23.0	22.9	20.7	22.5	26.7
ASIA-PACIFIC																	
AUSTRALIA	17.4	24.8	34.2	37.7	38.0	32.5	32.3	32.0	31.0	31.0	30.0	18.7	17.8	17.7	17.9	18.2	18.7
BANGLADESH	0.0	0.0	0.0	0.0	10.0	10.0	8.0	8.0	8.0	8.0	8.0	7.0	7.0	7.0	7.0	11.0	12.7
INDIA	3.0	1.5	2.3	2.0	2.5	2.4	3.5	3.5	3.5	9.3	12.0	12.4	14.5	14.0	13.6	14.9	17.6
MALAYSIA	6.0	7.5	10.0	13.0	15.0	15.0	15.0	17.0	17.0	17.6	15.0	19.0	34.0	40.0	50.0	52.7	49.4
PAKISTAN	20.0	19.5	16.0	10.1	16.0	16.4	15.8	15.5	16.0	15.8	15.1	16.4	18.5	15.8	15.8	15.4	18.7
NEW ZEALAND	6.5	6.0	17.0	15.0	5.0	5.0	6.2	6.0	6.0	6.0	6.1	6.0	5.5	5.5	5.4	5.5	5.7
OTHER ASIA-PAC	5.2	6.0	6.2	13.4	14.4	15.3	15.2	16.7	14.4	17.1	16.6	20.7	19.3	17.2	15.1	15.4	26.4
SUBTOTAL	53.3	65.3	95.7	99.2	100.9	96.6	96.0	98.7	95.9	104.2	102.8	100.2	116.6	118.0	126.2	133.9	149.2
MIDDLE EAST	7.9	7.9	7.6	6.9	9.7	9.3	6.7	8.6	11.0	13.0	13.5	15.1	12.0	12.9	16.0	14.7	20.5
TOTAL NON-OPEC	583.0	612.3	661.8	670.0	675.5	606.7	569.1	587.4	594.9	643.2	679.6	695.4	738.9	728.0	786.8	822.3	838.1
OPEC																	
IRAN	214.0	206.0	200.0	270.0	330.0	329.5	330.0	500.0	500.0	490.0	485.0	484.0	482.6	480.0	478.6	470.0	450.0
IRAQ	18.5	22.0	25.0	22.0	27.5	27.1	27.0	28.0	27.0	27.5	27.5	27.3	28.0	29.0	29.0	29.0	28.0
KUWAIT +	62.0	39.0	34.0	34.5	33.0	33.6	34.2	34.0	33.0	33.5	33.2	34.7	34.1	35.2	39.6	36.6	41.2
QATAR	8.0	8.0	8.0	8.0	8.0	7.5	27.5	40.0	40.0	40.0	40.0	40.0	42.0	42.0	42.0	140.0	152.0
SAUDI ARABIA +	53.5	56.0	53.0	54.9	58.0	104.0	65.5	87.5	94.0	95.7	112.4	108.2	121.2	125.2	127.6	125.1	130.2
UNITED ARAB EMIRATES	10.3	11.0	13.0	15.0	23.0	23.0	23.2	21.5	21.6	28.5	28.0	23.3	28.6	30.0	31.6	32.4	103.4
MIDDLE EAST	346.3	336.0	336.6	404.4	483.1	529.5	507.4	711.0	719.6	727.2	730.9	747.5	757.3	762.2	765.0	841.1	904.8
ALGERIA	141.0	104.5	105.0	105.9	129.0	126.0	125.0	125.0	105.0	132.0	131.5	130.9	111.3	110.2	109.1	107.1	106.0
GABON	7.0	6.5	7.0	6.5	7.0	2.5	2.5	2.5	2.4	0.5	0.5	0.5	0.5	0.5	0.6	0.4	0.5
LIBYA	30.0	29.5	27.5	27.0	26.5	26.3	25.0	25.7	24.2	24.0	23.0	23.2	23.5	23.4	23.2	23.4	23.2
NIGERIA	6.0	40.0	40.0	40.0	45.0	44.3	44.0	43.0	42.0	41.4	41.0	40.5	32.4	34.0	35.6	47.0	47.0
AFRICA	184.0	182.5	179.5	179.4	207.5	199.1	198.1	196.2	173.6	197.9	196.0	195.1	168.7	168.9	168.5	178.9	176.7
ECUADOR	5.0	4.0	5.0	5.0	5.0	5.0	5.0	5.0	4.0	4.0	4.0	4.3	4.1	3.5	3.0	4.1	4.1
INDONESIA	3.0	4.5	5.5	15.0	15.0	15.0	24.0	24.0	24.0	24.0	23.5	27.4	29.6	30.2	40.0	35.6	49.0
VENEZUELA	27.0	25.4	34.6	42.0	43.0	42.0	40.7	41.0	41.0	42.0	42.0	47.0	54.1	54.5	52.4	50.1	59.0
OTHER OPEC	35.0	33.9	45.1	62.0	63.0	62.0	69.7	70.0	69.0	70.0	69.5	78.7	87.8	88.2	95.4	90.0	112.5
TOTAL OPEC	565.3	554.4	561.2	647.8	753.6	790.6	775.2	977.2	962.2	995.9	1005.2	1021.3	1013.8	1019.3	1029.9	1119.0	1192.0
TOTAL FREE WORLD	1148.3	1166.7	1223.0	1297.8	1429.1	1397.3	1344.3	1564.6	1557.1	1639.1	1684.6	1716.7	1749.7	1753.3	1816.7	1938.1	2030.1
COMMUNIST COUNTRIES																	
USSR	426.0	546.0	633.4	706.0	872.0	880.0	918.0	920.0	916.0	900.0	920.0	1160.0	1240.0	1400.0	1450.0	1300.0	1250.0
EASTERN EUROPE	8.5	8.0	8.0	9.4	9.0	10.0	10.0	10.0	10.0	10.0	9.4	10.3	14.0	14.5	14.5	14.0	15.0
CHINA	6.0	4.0	21.0	20.0	25.0	25.0	25.0	25.0	25.0	25.0	24.5	24.4	29.8	30.3	30.0	30.0	30.0
TOTAL COMMUNIST	438.5	558.0	662.4	735.4	906.0	835.0	953.0	955.0	951.0	935.0	953.9	1194.7	1283.8	1444.8	1497.4	1344.0	1295.0
TOTAL WHOLE WORLD	1586.8	1724.7	1887.4	2033.2	2335.1	2232.3	2297.3	2519.6	2562.1	2574.1	2638.5	2911.4	3033.5	3200.1	3314.1	3484.1	3625.9

Table 3.3

HISTORICAL WORLD NATURAL GAS RESERVES (AT YEAR-END)

(Billions [10^9] barrels of crude oil equivalent)

	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986
NON-OPEC																	
WESTERN HEMISPHERE																	
UNITED STATES	45.3	44.1	44.4	42.3	42.7	36.8	37.6	35.9	35.0	33.2	32.6	33.8	34.9	33.8	33.8	33.7	31.7
CANADA	10.3	9.3	9.4	8.6	9.0	9.1	9.4	9.9	10.1	10.6	10.9	13.4	14.6	13.5	13.0	17.0	17.0
MEXICO	1.7	2.0	2.0	1.9	2.6	2.1	2.1	5.1	5.5	10.1	11.0	12.9	13.0	12.9	13.2	13.2	13.1
ARGENTINA	1.3	1.3	1.5	1.4	1.3	1.2	1.2	1.4	2.1	2.6	3.8	4.0	4.3	4.2	4.2	4.0	3.9
TRINIDAD/TOBAGO	0.6	0.9	1.3	0.9	1.0	0.7	0.6	1.5	1.4	1.4	2.1	1.8	1.9	2.2	1.8	1.8	1.8
OTHER WEST HEMISPH	3.2	2.9	2.8	3.5	4.1	3.5	2.6	2.7	2.7	2.6	2.6	2.6	2.8	2.6	2.4	2.6	2.9
SUBTOTAL	62.7	62.4	63.4	58.6	60.6	53.3	53.6	56.5	56.8	64.5	67.0	70.6	73.4	71.3	71.2	72.3	70.4
WESTERN EUROPE																	
NORWAY	0.5	1.7	2.1	3.1	4.2	4.3	3.2	3.4	4.1	4.0	7.3	8.4	9.9	10.1	15.2	17.8	17.6
NETHERLANDS	14.2	14.2	15.0	15.7	14.3	12.0	10.6	10.3	10.6	10.2	10.6	9.5	8.9	8.6	11.7	11.5	12.0
UNITED KINGDOM	6.2	6.8	7.7	8.5	8.5	8.3	5.1	5.0	4.6	4.3	4.2	4.4	4.3	4.3	4.8	5.6	5.7
WEST GERMANY	2.6	2.4	2.2	2.1	2.0	1.4	1.3	1.2	1.1	1.1	1.0	1.1	1.1	1.2	1.0	1.1	1.1
OTHER WEST EUROPE	2.4	2.8	3.0	2.8	3.7	4.7	4.1	3.7	4.1	3.6	4.1	2.3	2.6	2.8	2.6	2.7	2.8
SUBTOTAL	25.2	27.9	30.5	33.1	34.7	30.9	28.3	23.6	24.5	23.1	27.2	25.8	26.8	26.9	35.3	38.7	39.3
AFRICA	1.3	1.8	1.6	1.9	1.3	1.6	1.9	1.9	2.2	2.3	2.0	2.8	4.1	3.9	3.5	3.8	4.6
ASIA-PACIFIC																	
AUSTRALIA	2.2	4.2	4.2	4.6	4.5	5.6	5.5	5.5	5.3	5.3	5.1	3.2	3.0	3.0	3.1	3.1	3.2
BANGLADESH	0.0	0.0	1.9	1.8	1.7	1.7	1.6	1.4	1.4	1.4	1.4	1.2	1.9	1.2	1.2	2.0	2.2
INDIA	0.5	0.3	0.4	0.3	0.4	0.4	0.6	0.6	0.6	1.6	2.1	2.1	2.5	2.5	2.6	2.9	3.0
MALAYSIA	1.0	1.3	1.7	2.2	2.6	2.6	2.6	2.9	2.9	2.9	2.6	5.2	5.8	6.2	8.5	9.0	8.4
PAKISTAN	3.0	3.3	3.7	3.7	2.7	2.8	2.7	2.6	2.7	2.7	2.6	2.8	3.2	2.7	2.7	2.6	3.2
NEW ZEALAND	1.1	1.0	2.9	2.6	0.9	0.9	1.1	1.0	1.0	1.0	1.0	1.0	0.9	0.9	0.9	0.9	1.0
OTHER ASIA-PAC	0.9	1.0	1.1	2.3	2.5	2.6	2.6	2.9	2.5	2.9	2.8	3.5	3.3	2.9	2.6	2.6	4.5
SUBTOTAL	9.1	11.2	16.4	17.0	17.2	16.5	16.4	16.9	16.4	17.8	17.6	17.1	19.9	21.5	21.6	23.2	25.5
MIDDLE EAST	1.0	1.0	1.3	1.2	1.7	1.0	1.1	1.5	1.9	2.2	2.3	2.6	2.1	2.2	2.8	2.5	3.5
TOTAL NON-OPEC	99.7	104.7	113.1	111.1	115.5	103.7	97.3	100.4	101.7	109.9	116.1	118.9	126.3	125.8	136.5	140.6	143.3
OPEC																	
IRAN	34.6	34.2	34.2	46.2	56.4	56.3	56.0	85.5	85.5	83.8	82.9	82.7	82.5	82.1	81.8	80.3	76.9
IRAQ	3.2	3.8	4.3	3.8	4.7	4.6	4.4	4.8	4.8	4.7	4.7	4.7	4.9	5.0	4.9	5.0	4.8
KUWAIT *	7.2	6.7	6.3	6.2	6.1	6.1	5.8	5.8	5.8	5.7	5.7	5.9	5.8	6.0	6.3	6.3	7.0
QATAR	1.0	1.0	1.0	1.4	1.4	1.3	4.7	6.8	6.8	10.3	10.3	10.3	10.6	10.6	10.6	25.3	26.0
SAUDI ARABIA *	9.1	9.6	9.2	9.4	10.1	10.3	11.2	15.0	16.5	16.4	19.2	20.2	20.7	21.4	21.8	21.4	22.3
UNITED ARAB EMIRATES	1.8	1.9	2.2	2.6	3.9	3.9	4.0	3.7	3.7	3.5	3.6	4.0	4.9	5.3	5.4	5.5	17.7
MIDDLE EAST	59.2	57.4	57.5	69.5	82.6	90.3	86.7	121.5	123.0	124.3	126.3	127.8	129.5	130.3	130.8	143.8	154.7
ALGERIA	24.1	18.2	17.9	18.1	22.1	21.5	21.3	21.4	17.9	22.6	22.5	22.4	19.0	18.8	18.6	18.3	18.1
GABON	1.2	1.1	1.2	1.1	1.2	0.8	0.8	0.8	0.8	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
LIBYA	5.1	5.0	4.7	4.6	4.5	4.5	4.5	4.4	4.1	4.1	4.1	4.0	3.7	3.7	3.6	3.7	3.6
NIGERIA	1.0	6.8	6.8	6.8	7.7	7.6	7.5	7.4	7.2	7.1	7.0	6.9	5.5	5.9	6.1	8.0	8.0
AFRICA	31.3	31.2	30.7	30.7	35.5	34.0	33.9	33.5	29.7	33.8	33.6	33.4	28.3	28.5	28.3	30.1	29.9
ECUADOR	0.9	1.0	0.9	0.9	0.9	0.9	0.9	0.9	0.7	0.7	0.7	0.7	0.7	0.6	0.5	0.7	0.7
INDONESIA	8.5	8.8	8.9	8.6	8.6	8.6	8.1	8.1	8.1	8.1	8.0	4.7	5.1	5.2	6.8	8.1	8.4
VENEZUELA	4.6	4.3	5.9	7.2	7.6	7.2	7.0	7.0	7.0	7.3	7.2	8.9	9.2	9.3	9.5	10.1	10.1
OTHER OPEC	6.0	6.1	7.7	10.6	10.8	10.6	11.9	12.0	11.8	12.1	11.9	13.5	15.0	15.1	16.8	16.9	19.2
TOTAL OPEC	96.6	98.8	95.9	110.7	128.8	125.1	122.5	167.0	164.5	170.2	171.8	174.6	172.8	173.9	176.1	190.7	203.8
TOTAL FREE WORLD	196.3	199.4	209.1	221.8	244.3	228.9	219.8	267.5	266.2	280.2	288.0	293.5	299.1	299.7	310.5	331.3	347.0
COMMUNIST COUNTRIES																	
USSR	72.8	93.3	108.6	120.7	128.8	136.8	156.9	157.3	155.6	153.8	157.3	198.3	212.0	229.3	247.9	256.4	265.0
EASTERN EUROPE	1.3	1.4	1.4	1.4	1.5	1.7	1.7	1.7	1.7	1.7	1.6	1.8	2.4	2.8	2.8	2.7	2.7
CHINA	6.7	6.7	3.6	3.6	4.3	4.3	4.3	4.3	4.3	4.3	4.2	4.2	5.1	5.2	5.3	5.1	5.1
TOTAL COMMUNIST	75.0	95.4	113.6	125.7	134.6	142.7	162.9	163.2	161.5	159.8	163.1	204.2	219.5	237.3	256.0	264.3	272.8
TOTAL WHOLE WORLD	271.2	294.8	322.6	347.4	378.9	371.6	382.7	430.7	427.7	440.0	451.0	497.7	518.5	547.0	566.5	595.6	619.8

* INCLUDES 1/2 NEUTRAL ZONE

SOURCE: SRI INTERNATIONAL

Table 3.4

WORLD NATURAL GAS MARKETED PRODUCTION
(Trillions [10^{12}] of cubic feet/year)

	1970	1975	1980	1985
WESTERN HEMISPHERE				
UNITED STATES	21.9	20.1	20.4	18.0
CANADA	2.3	3.1	2.7	1.9
LATIN AMERICA	1.3	1.7	3.3	2.7
SUBTOTAL	25.5	24.9	26.4	22.6
WESTERN EUROPE	2.8	6.0	6.7	8.7
AFRICA	0.1	0.7	0.9	1.2
ASIA-PACIFIC	0.5	0.9	2.6	3.4
MIDDLE EAST	0.5	1.4	1.2	1.6
TOTAL FREE WORLD	29.4	33.9	37.8	37.5
COMMUNIST COUNTRIES	8.7	13.3	21.1	30.3
TOTAL WHOLE WORLD	38.1	47.2	58.9	67.8

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* INCLUDES 1/2 NEUTRAL ZONE

SOURCE: SRI INTERNATIONAL

Table 3.5

WORLD NATURAL GAS RESERVES/PRODUCTION
(Years)

	1970	1975	1980	1985
WESTERN HEMISPHERE				
UNITED STATES	12.1	10.7	9.4	10.9
CANADA	26.3	17.2	32.3	52.5
LATIN AMERICA	56.2	53.2	48.4	70.1
SUBTOTAL	15.6	14.4	16.6	21.5
WESTERN EUROPE	52.8	30.2	23.8	26.0
AFRICA	1915.0	295.9	231.7	165.3
ASIA-PACIFIC	112.6	124.0	48.6	50.4
MIDDLE EAST	708.4	384.9	627.0	534.9
TOTAL FREE WORLD	39.1	41.2	44.6	51.7
COMMUNIST COUNTRIES	50.4	62.8	45.2	51.0
TOTAL WHOLE WORLD	41.6	47.3	44.8	51.4

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* INCLUDES 1/2 NEUTRAL ZONE

SOURCE: SRI INTERNATIONAL

Figure 3.1

WORLD NATURAL GAS RESERVES, 1970-1985

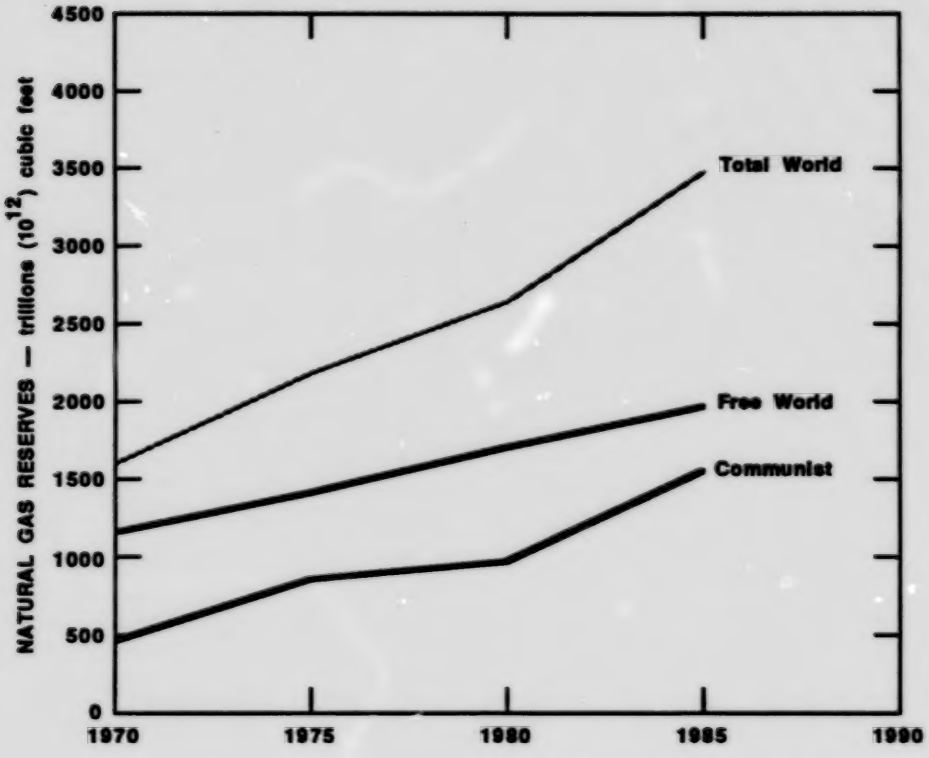


Figure 3.2

TOTAL WORLD NATURAL GAS AND CRUDE OIL RESERVES, 1970-1986

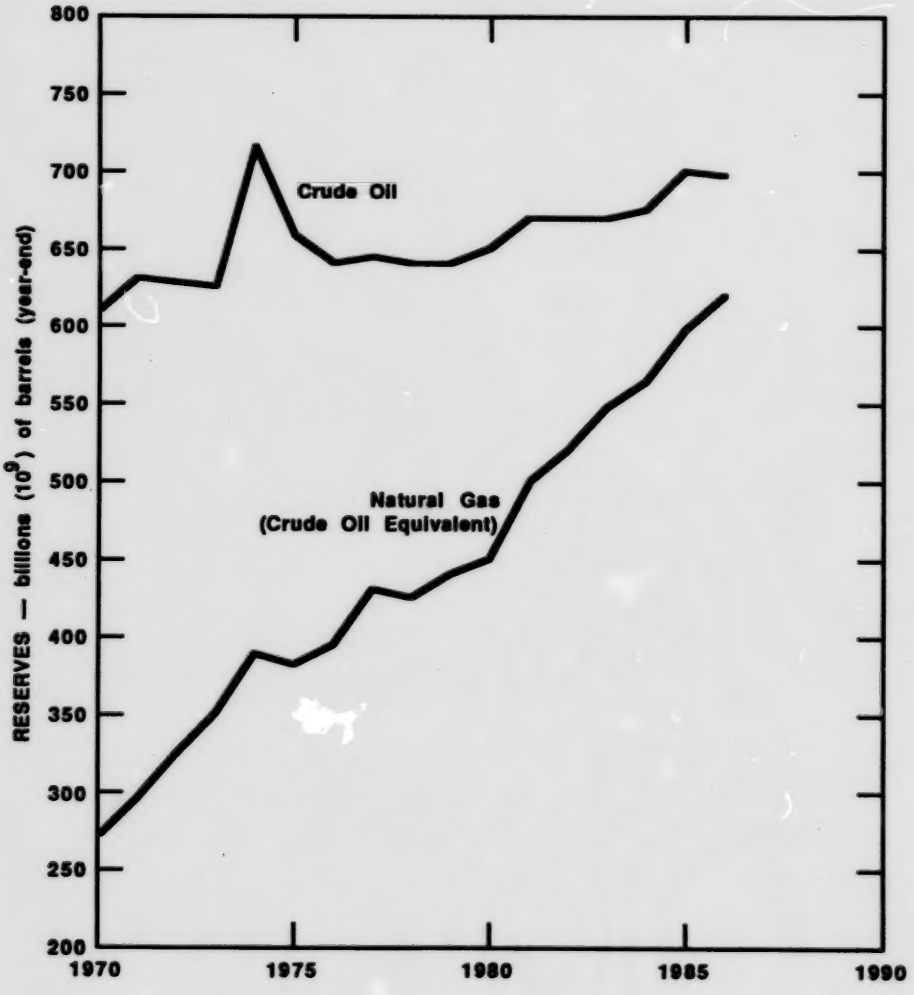


Figure 3.3

WORLD NATURAL GAS MARKETED PRODUCTION, 1950-1985

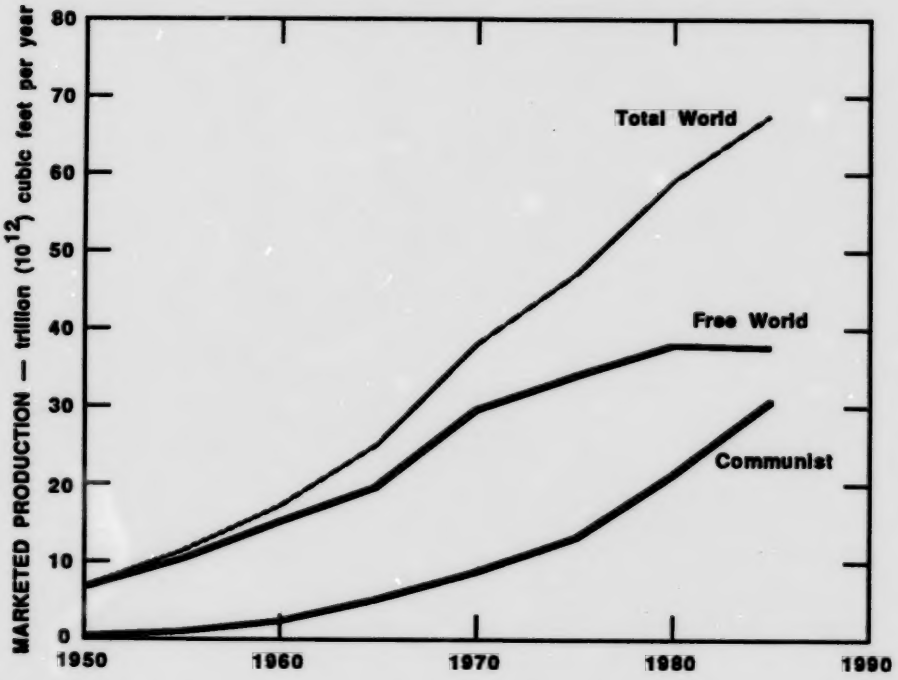
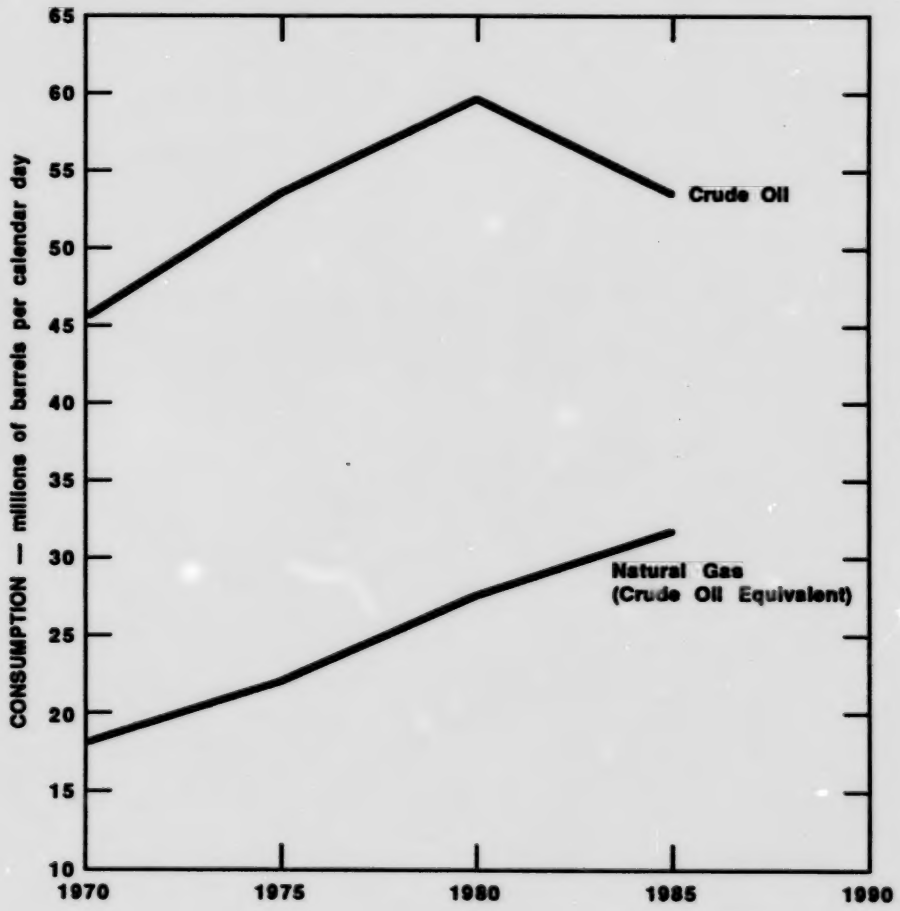


Figure 3.4

TOTAL WORLD NATURAL GAS AND CRUDE OIL CONSUMPTION, 1970-1985



4 METHANE ACTIVATION CATALYSIS AND RELATED RESEARCH

Introduction

Both industrial and academic laboratories have intensively studied the activation and direct catalytic conversion of methane into liquid fuels over the past several years. Much of the research has sought to discover catalytic materials of high selectivity for hydrocarbons or oxygenated hydrocarbons such as alcohols or aldehydes. Catalysts examined for methane activation include elements that cover a wide range in the periodic table but exclude those metals and metal oxides (e.g., platinum and cobalt oxide) known to be good total oxidation catalysts.

Because methane is less reactive than other hydrocarbons, the conditions required for its activation are more severe than those for the partial oxidation of higher alkanes. The formation of oxygenates [1] by the reaction of methane with oxygen over molybdena, molybdenates, or other molybdenum, tungsten, or vanadium oxide based partial oxidation catalysts proceeds at moderate pressure (20 to 50 atm) and moderate temperature (650–850K). The highest reported selectivity is 80% methanol and formaldehyde, but in general the yield of oxygenates is quite low per pass (<8% on a carbon basis) because of the high methane-to-oxygen ratio of the feed gas required for high selectivity. The coupling of methane to form light alkanes and alkenes proceeds at low pressure (1 to 10 atm) and higher temperature (900K and above) under these conditions but over different catalysts. Attempts to catalytically convert methane into higher hydrocarbons have thus far been more successful than conversion into oxygenates in terms of both selectivity (>95% versus 80%) and yields (>20% versus 8%). The following discussion of methane activation catalysts addresses methane coupling processes.

Methane Coupling Research

The key property of a successful catalyst for oxidative dimerization of methane is high selectivity for hydrocarbons, or--perhaps more accurately stated--low selectivity for the carbon oxides, CO and CO_2. Because the products of the reaction are more easily activated than methane, the greatest selectivity occurs under conditions that give low conversion. Conditions that favor high selectivity in addition to high space velocity are high temperature, low oxygen partial pressure, and high methane partial pressure; high methane conversion is favored by low space velocity and high oxygen partial pressure. In the continuous flow reaction of methane with dilute oxygen, the selectivity of a given catalyst consistently declines with increasing single pass conversion (see Figures 4.1 and 4.2), despite wide differences in reaction conditions and catalyst. However, even at the lowest methane conversion, hydrocarbon selectivity varies greatly (from >99% to <1%) with the nature of the catalyst.

Several classes of catalysts have significant selectivity for methane activation. They include alkaline earth oxides, rare earth oxides, manganese oxide, and oxides of the soft metals such as lead, cadmium, bismuth, and antimony. Manganese oxide is the exception among the

transition metal oxides in that it has significant hydrocarbon selectivity. Different explanations have been offered to describe how each class of catalyst activates methane.

As a result of electron paramagnetic resonance (EPR) measurements they have made, Lunsford et al. have proposed that the active center on the surfaces of the alkaline earth oxide [2–5] and lanthanum oxide [6] are oxygen anion radicals (O^-). The enhanced C_2 hydrocarbon selectivity of alkali–promoted alkaline earth catalysts correlates well with the increased concentration of alkali–oxygen radical anion centers [Me^+O^-] determined by the EPR signals of quenched Li promoted MgO [3–5] and Na promoted CaO [5,7] catalysts.

The lanthanide rare earth oxides also show good selectivity for higher hydrocarbons, although considerable variance has been observed in the low conversion selectivity. Lunsford et al. [6] report moderate selectivity for La_2O_3, despite a high yield of methyl radicals trapped downstream. The moderate selectivity relative to Li/MgO was attributed to the higher rate of oxidation of product hydrocarbons. Otsuka et al. [9–11] have studied the methane oxidative dimerization selectivity of trivalent oxides across the lanthanide series (La, Ce, Pr, Nd, Sm, ..., Yb, and Lu), as well as Sr and Y, and report high activity per unit of surface area and good selectivity for Sm_2O_3 and La_2O_3, but low activity for Pr_2O_3; Jones et al. [8,12] report high activity for sodium–promoted praseodymium oxide, which they attribute to the formation of a partially reduced oxide phase, Pr_6O_{11}.

The low stability of the basic oxides of the Group III–V soft metals is thought [13–16] to favor a redox process in which methane reduces the surface oxide and gaseous O_2 replaces it. Obviously, for the Redox process, high thermochemical potential and high $O^=$ mobility are necessary for sustained methane activation. The basic rather than acidic nature of these oxides may contribute to their selectivity for high hydrocarbons. A recent study by Baerns et al. [17] found that increased acidity of the support decreased the C_2^+ selectivity of PbO.

Alkali promoters are widely used with methane activation catalysts. Lunsford et al. [3,4,6] have proposed that alkali dissolves in the near surface layers of the alkaline earth catalysts and forms the active O^- centers as seen with EPR spectroscopy. However the EPR signals may reflect formation of bulk defects rather than surface O^- centers. The large amounts of promoter used (to 30 wt%) with MgO and CaO are known [18] to increase basic strength with little effect on O^- surface concentration as determined by titration. Alkali promoters are effective with methane activation catalysts other than alkaline earth oxides, and often increase selectivity without correspondingly increasingly the methane conversion rate. Emesh and Amenomiya [16] have recently shown that sodium–promoted bismuth oxide has much greater selectivity than unpromoted Bi_2O_3. On silica–supported manganese oxide, however, the promoting effect of Na has been attributed [8] to facilitated formation of Mn_7SiO_{12}, which was considered to be the active phase. Akai et al. [19], have shown that strontium carbonate has the highest selectivity reported (99.5% at 2.5% conversion), supporting the concept that increased selectivity is correlated with increased basic strength. Thus alkali may act more to suppress hydrocarbon oxidation than to promote methane conversion.

The understanding of the mechanism of hydrocarbon product formation will help to define the ultimate selectivity of the coupling process and aid the development of superior catalysts by indicating the essential properties of the active surface phase. Two divergent mechanisms have been proposed for the oxidative coupling of methane to higher hydrocarbons. Work on PbO and related catalysts [13], suggests that methane interacts with surface oxygen atoms in

the oxide layer to produce adsorbed methyl radicals and an hydroxide ion in a Langmuir–Hinshelwood step:

(1) $CH_4\ (g) + O\ (a) \rightarrow CH_3\ (a) + OH\ (a)$,

where (*g*) refers to gas phase and (*a*) to adsorbed molecules. No attempt is made to describe the electron transfer steps in the mechanism presented here. Adjacent adsorbed methyl radicals interact to associatively produce a desorbing ethane molecule:

(2) $CH_3\ (a) + CH_3\ (a) \rightarrow C_2H_6\ (g)$.

Product ethane reacts with the oxide surface, dissociatively adsorbs, and produces ethylene, butane, or propane by associative reaction with adjacent oxygen, methyl, or ethyl radicals:

(3) $C_2H_6\ (g) + O\ (a) \rightarrow C_2H_5\ (a) + OH\ (a)$,

(4) $C_2H_5\ (a) + O\ (a) \rightarrow C_2H_4\ (g) + OH\ (a)$,

(5) $C_2H_5\ (a) + CH_3\ (a) \rightarrow C_3H_8\ (g)$,

(6) $C_2H_5\ (a) + C_2H_5\ (a) \rightarrow C_4H_{10}\ (g)$.

Formation of the active oxygen species and the desorption of water completes the mechanism:

(7) $O_2\ (g) \rightarrow O\ (a) + O\ (a)$,

(8) $OH\ (a) + OH\ (a) \rightarrow H_2O\ (g) + O\ (a)$.

Modifications to this mechanism include (a) the postulate that O^- species at the oxide surface are the activating centers [11] and (b) the suggestions [17] that Bronstead acid centers lead to the formation of H_2 and adsorbed CH_3^+ carbonium ions that decompose into by-product CO.

The other mechanism [2–5,20] proposes that methane reacts with surface O^- centers in an Eley–Rideal step to produce surface OH^- anions and a gas-phase methyl radical. A similar step would apply to activation of higher hydrocarbon products, thus:

(9) $CH_4\ (g) + O\ (a) \rightarrow CH_3\ (g) + OH\ (a)$,

(10) $C_2H_6\ (g) + O\ (a) \rightarrow C_2H_5\ (g) + OH\ (a)$.

This postulate is based on direct observation of methyl radicals downstream of catalyst beds of lithium-promoted MgO [20] and lanthanum oxide [6] during methane conversions. The high temperatures required to achieve significant methane conversion and the observation of a product distribution consistent with gas-phase free radical chemistry with a variety of different methane activation catalysts also support this mechanism.

The question of which which mechanism applies to the initial methane activation step has important technological implications. If the second-order recombination of gas-phase methyl radicals produces higher hydrocarbons, the catalyst must generate methyl radicals at a high rate, or it must be relatively passive with respect to the oxidation of hydrocarbon radicals to

achieve high selectivity. Furthermore, the selectivity could be seriously impaired by the reaction of methyl radicals with gaseous oxygen [4], even with negligible oxidation of the radicals at the surfaces of the catalyst. On the other hand, if a branching step at the surface controls the selectivity, high selectivity may be possible with relatively high oxygen partial pressure. Detailed kinetic studies should be conducted to distinguish between the two mechanisms.

Because many potential catalyst have already been examined for methane activation, current research is focusing on the characterization of selective catalyst and the kinetics of the oxidative coupling reactions. Lunsford et al. [4] have studied the competitive coupling reactions of methane and ethane, in addition to the results of experiments isolating methyl radicals, and have found that ethane conversion to ethylene competes with methane activation, thereby lowering the steady-state concentration of active oxygen centers at the MgO surface. Otsuka et al. [11] have studied the effect of O_2 partial pressure on the reaction kinetics and found a large effect on rate of methane conversion rate but, encouragingly, a smaller effect on higher hydrocarbon selectivity. Additional detailed kinetic studies of the catalytic conversion of methane and its product hydrocarbons such as ethylene and ethane under controlled differential reaction conditions are needed to provide a better experimental basis for understanding the reaction mechanism.

Important questions about the activation process remain, particularly about the inherent low conversion selectivity of a catalyst and the reasons for the decline in selectivity of all catalysts as conversion increases. Additional kinetic studies should provide answers in the next several years. Gas-phase reaction models developed for methane pyrolysis and low oxygen combustion can be applied to predict the fate of methyl and ethyl radicals, and to judge the effect of homogeneous reactions on the product distribution. Transient kinetic experiments with isotopically labeled compounds and adsorption/desorption experiments could test the individual steps in the reaction mechanism, thereby identifying the key reactive intermediates and the rate determining reaction steps.

More detailed characterizations of methane activation catalysts will provide a better understanding of the essential properties of oxide surfaces that provide maximum selectivity and help guide the development of technologically important catalyst systems. Additional EPR experiments may verify the essential role of oxygen anion radicals as centers of activation. Examination of the microscopic structure and phase composition of active catalysts may identify those complex oxide phases of promoted or supported catalysts responsible for high activity and high selectivity for C_2^+ hydrocarbons. Given the rapid advance in the discovery of selective catalysts for oxidative methane during the past 5 years and the intensity of current research, it is likely that catalysts will soon be developed that successfully achieve both high selectivity (>90%) and moderate yield per pass (>15% on a carbon basis).

A Summary of Methane Activation Catalysis and Related Research

Research activities are summarized in the following tables:

Table 4.1 Summary of Selected ARCO Patents on Methane Conversion

Table 4.2 Summary of Selected Mobil Research on Light Hydrocarbon Conversion

Table 4.3 Summary of Selected Research in the United States on Light Hydrocarbon Conversion

Table 4.4 Summary of Selected Australian Research on Methane Conversion

Table 4.5 Summary of Selected Canadian Research on Light Hydrocarbon Conversion

Table 4.6 Summary of Selected Japanese Research on Light Hydrocarbon Conversion.

Table 4.1

SUMMARY OF SELECTED ARCO PATENTS ON METHANE CONVERSION

Developer	Patent Reference	Feedstock	Catalyst	Temperature (°C)	Pressure (bar)	Contact Time	Product	Conversion (mol%)	Selectivity to C_{2+} (mol%)
ARCO	U.S. 4499322	CH_4	Oxide of Mn, Sn, In, Ge, Pb, Sb, or Bi and alkali metal promoter	800	1	2 min @ SV = 300–1200/h	C_2-C_7 hydrocarbons	5–60	30–90
ARCO	U.S. 4517398	CH_4	Oxide(s) of Mn, In, Sn, Ge, Pb, Sb, and/or Bi on hydroxylated magnesia support	800–850	1	2 min @ SV = 600–1200/h	C_2-C_7 hydrocarbons	10–40	20–88
ARCO	U.S. 4547611	CH_4	Same as U.S. 4517398	800	1	2 min @ SV = 1200/h	C_2-C_7 hydrocarbons	8–21	43–90
ARCO (5 patents)	U.S. 4443644 to U.S. 4443648	CH_4	Oxides of Sb, Ge, Bi, Pb, and In	700–800	1	to30 min @ SV = 88–880/h	C_2-C_7 hydrocarbons	0–5	10–100
ARCO	U.S. 4443649	CH_4; CH_4, C_2H_4 mix; CH_4, C_2H_6 mix	Oxide of Mn and aromatics	650–800	1	to 30 min @ SV = 300–1200/h	C_2-C_7 hydrocarbons	1–30	60–100
ARCO	U.S. 4444984	CH_4	Oxide of Sn	700–800	1	to 15 min @ SV = 600/h	C_2-C_7 hydrocarbons	0–10	25–100
ARCO	U.S. 4544784	CH_4; CH_4, CH_3Cl mix	Reducible metal oxide and halide promoter	700–800	1	to 30 min @ SV = 600–2400/h	C_2-C_7 hydrocarbons	0.3–30	2–93
ARCO	U.S. 4554395	CH_4	Reducible metal @ SV = 435–3120/h	700–800 hydrocarbons	1 to 8	to 30 min	C_2-C_7	0.3–14	16–85

Table 4.2

SUMMARY OF SELECTED MOBIL RESEARCH ON LIGHT HYDROCARBON CONVERSION

Reference	Feedstock	Catalyst	Temperature (°C)	Pressure (bar)	Contact Time	Product	Conversion	Selectivity
U.S. 4350835	C_2H_6	Ga-impregnated HZSM-5	565-621	1	To 3 h @ WHSV = 0.5/h	Aromatics (BTX), light olefin gases, and light paraffin gases	11 to 33 wt%	58 to 64 g of aromatics per 100 g of C_2H_6 converted
		Zn-Cu impregnated HZSM-5	621	1	To 40 min @ WHSV = 0.43 to 0.65/h	Same as above	32 to 35 wt%	3[illegible] g of [illegible] per 100 g of C_2H_6 converted
U.S. 4100218	Olefin-rich (C_2H_4) effluent from ethane cracking furnace	HZSM-5	316-650	1-13	WHSV = 1 to 10/h	Gasoline and light gases	Not given	As much as 85 g of LPG and gasoline from 100 g of ethane fed to the cracking furnace
	C_2H_4	HZSM-5(B)	343-470	1	WHSV = 1/h	Light gases, LPG, gasoline, and aromatics	99 wt%	As much as 70 wt% yield of 99 R+0 gasoline; 16-35 g of BTX/100 g of C_2= converted
	C2H4	Zn-exchanged HZSM-5	470	1	WHSV = 1/h	Same as above	99 wt%	57 g of BTX/100 g of C_2= converted 24 g of LPG/100 g of C_2= converted
W.E Garwood, paper presented at the 184th Meeting of the American Chemical Society, Kansas City, MO (September 12-17, 1982)	C2-C10 olefins	HZSM-5	232-388	1-100	WHSV = 0.4 to 2.7/h	Paraffins, aromatics, and higher-boiling olefins	10 to 90 wt%	For propylene: 37 g of aromatics/100 g of C_3= converted; 48 g total C_6+/100 g of C_3= converted
U.S. 4456779 U.S. 4456781 *Hydrocarbon Processing*, p. 72 (September 1985)	C_2-C_4 olefins	HZSM-5	230-260 distillate 230-375 gasoline	40 to 70 (distillate) 4 to 30 (gasoline)	LHSV = 0.5 to 1/h (distillate) LHSV = 0.5 to 2/h (gasoline)	LPG, gasoline, jet fuel, and distillate	50% for ethene;95% for propene; 85% for butene-1; 75% for pentene-1	Maximum gasoline yield (C_5+):57 wt%; maximum distillate yield (330°F+): 69-79 wt%

Table 4.3

SUMMARY OF SELECTED RESEARCH IN THE UNITED STATES ON LIGHT HYDROCARBON CONVERSION

Developer	Reference	Feedstock	Catalyst	Temperature (°C)	Pressure (bar)	Contact Time	Product	Conversion	Selectivity
Ito and Lunsford, Texas A&M	*Nature*, 314 (6013), 721 (May 25, 1985)	CH_4, O_2, He (diluent)	Li/MgO	600–770	1	SV = 80/min	C_2H_4, C_2H_6, CO_2, CO, CH_3OH, HCHO	4% to 43%	35% to 45% conversion to C_2+, based on CH_4 converted
Ito, Wang, Lin, and Lunsford Texas A&M	*American Chemical Society Journal*, 107, 5062 (1985)	CH_4, O_2, He (diluent)	Li/MgO	600–770	1	SV = 20 to 80/min	Same as above	25% to 51%	35% to 61% conversion to C_2+, based on CH_4 converted
Keller and Bhasin, Union Carbide	*Journal of, Catalysis*, 73, 9 (1982)	Pulsed flow of air, CH_4, N_2	Numerous supported metal oxides	500–1000	1	air: 60 sec @ WHSV = 0.58/h CH_4: 30 @ WHSV = 0.32/h	C_2H_4, C_2H_6, CO_2	0% to 11%	0–45% conversion to C_2+, based on CH_4 converted (reactor walls thought to be catalytically active)
Mitchell and Waghorne, Exxon	U.S. 4239658	CH_4	Supported catalyst-reagent, Ca, Cr, Pt with Zn	700	1	30 min	C_2 to C_4 olefins and paraffins; C_6H_6; coke	0.3 to 12 mol%	<20 mol% conversion to C_6H_6, based on CH_4 converted; <80 mol% conversion to C_2 to C_4 gases, based on CH_4 converted
Fox, Curatolo, and Pesa, Amoco	U.S. 4450310	CH_4	13 mixed metal oxide catalysts	800–900	1	To 3.5 @ SV = 0.43 to 2.0/min	C_2H_4, C_2H_6, C_3H_6, H_2	1.3 to 29 mol%	0.8 to 25 mol% C_2+, based on CH_4 converted

Table 4.4

SUMMARY OF SELECTED AUSTRALIAN RESEARCH ON METHANE CONVERSION

Developer	Reference	Feedstock	Oxidant	Catalyst	Temperature (°C)	Pressure (bar)	Contact Time	Product	Conversion (%)	Selectivity
CSIRO Division of of Materials Science	*Applied Catalysis*, 19, 141-152 (1985)	CH_4	Dioxygen	Metal oxides H-ZXMS	222-518 357-461	1	To 200 min @ SV = 1,080 to 12,0000/h	CO_2,CO	0.1 to 19	0% C_2+
			Nitrous oxide			1	To 200 min @ SV = 14,570 to 53,570/h	Carbon oxides, methanol, formaldehyde, olefins, aromatics	0.1 to 2.7	15 to 32 mol% C_2+
CSIRO Division of Materials Science	*Applied Catalysis*, 19, 1-11 (1985)	CH_4	O_2	Oxides of Mo, Fe,Zn,U,V	431-493	50-54	SV = 23,200 to 47,600/h	Methanol formaldehyde, carbon oxides	2.1 to 3.5	21 to 80 mol% methanol and HCHO
		CH4	O_2, Cu		141-184			Methanol, formaldehyde, carbon oxides	1.6 to 3.5	25 to 77 mol% methanol and HCHO

Table 4.5

SUMMARY OF SELECTED CANADIAN RESEARCH ON LIGHT HYDROCARBON CONVERSION

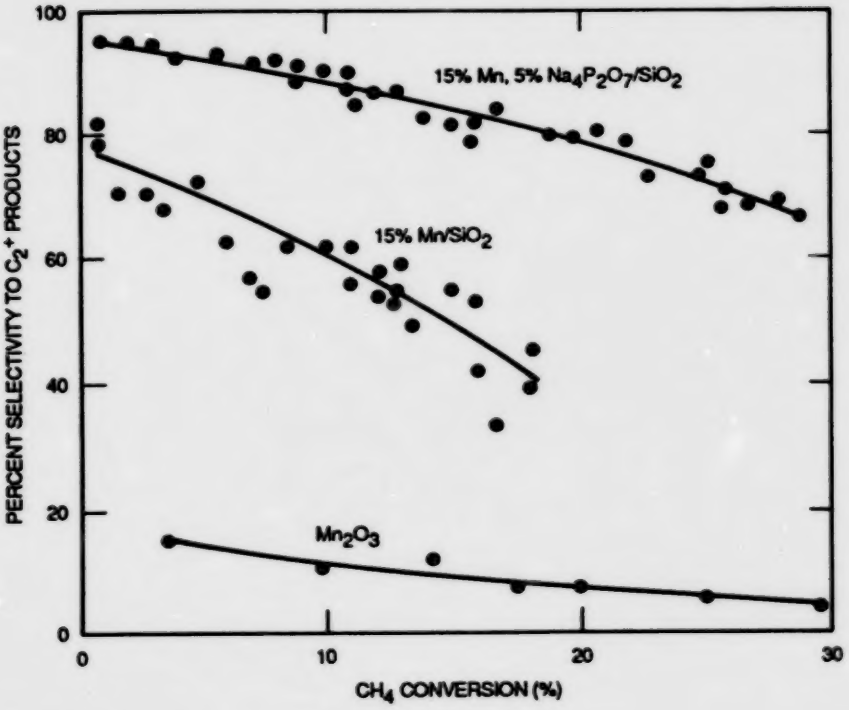
Developer	Reference	Feedstock	Catalyst	Temperature (°C)	Pressure (bar)	Contact Time	Product	Conversion (%)	Selectivity to C_2+ (mol%)
Hunter, Gesser, and Morton, University of Manitoba	6th International Symposium on on Alcohol Fuel Technology, Ottawa (May 1984)	CH_4 and O_2	None (SS reactor used)	450	50–125	Estimated 15–60 min @ SV = 5 to 20/min	CO, CO_2, C_2H6, CH_3OH	Not given, but probably low	12% to 81% CH_3OH; yield based on CH_4 converted
Amenomiya and Emesh, NRC, Ottawa	35th Canadian Chemical Engineering Conference, Calgary (October 1985)	CH_4 (50%), Air (25%), He(25%),	Oxides of Groups IIIa, IVa, and Va supported metals	550–700	Not given, but estimated at 1	Up to 100 h @ SV = 5 to 10/min	CO_2, H_2O, C_2 hydrocarbons, trace of C_3+ hydrocarbons	0.6 to15	0.9% to 28% conversion to C_2+, based on CH_4 reacted
Gesser, Hunter, and Prakash, Univeristy of Manitoba	*Chemical Review*, 85, 4 (August 1985)	Numerous, including, natural gas/air, natural gas/O_2, CH_4/O_2, CH_4, O_2, H_2	Numerous (17 experimental results quoted)	250–500	1.5–300	SV = 0.6 to 830/min	CH_3OH, HCHO	1.9 to 21	1% to 74% conversion to CH_3OH, based on CH_4 converted
		CH_4, O_2, Cl_2	Cr on pumice	430	1.5		CH_3OH, HCHO	18.3	40.2% conversion to CH_3OH, based on CH_4 converted

Table 4.6

SUMMARY OF SELECTED JAPANESE RESEARCH ON LIGHT HYDROCARBON CONVERSION

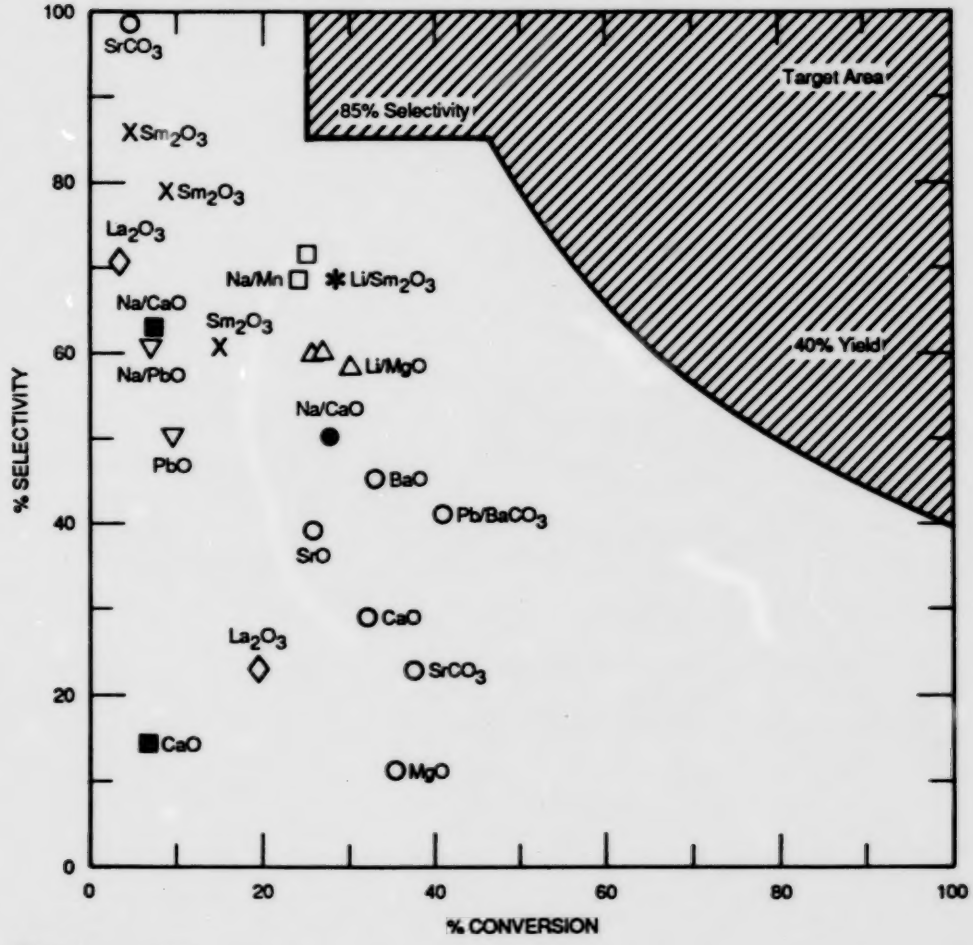
Developer	Reference	Feedstock	Catalyst	Temperature (°C)	Pressure (bar)	Contact Time	Product	Conversion	Selectivity
T. Inui, Kyoto University	*Journal of Catalysis*, 90, 366-367 (1984)	C_3H_8 (20 vol% in N_2)	Pt/HZSM-5	300-550	1	SV = 2,000/h	Light gases, aromatics, aliphatics	0-99 wt%	Maximum 25 g aromatics per 100 g of C_3 converted
			HZSM-5	300-550	1	SV = 2,000/h	Light gases, aromatics aliphatics	0-20 wt%	Reported as "low"
K. Ogura, Yamaguchi University	*Nature*, 319, 23 (January 1986)	CH_4	Pt electrode in aqueous KCl and illumination by quartz lamp	25	1	3 h	CH_3OH, CH_3Cl, CH_2Cl_2, CCl_4	Not reported, but estimated at 15 mol%	Not reported, but estimated at less than 3 mols of CH_3OH per 100 mols of CH_4 converted
K. Otsuka, Tokyo Institute of Technology	*Chemical Letters*, 499 (1985)	CH_4 & O_2 in He	25 metal oxides	700	1	Not given	C_2H_6, C_2H_4 CO_2, H_2O	Not given	>75 mol% conversion to C_2H_4 and C_2H_6 for about one-third of the rare earth oxides

Figure 4.1
METHANE CONVERSION TO HIGHER HYDROCARBONS



SOURCE: Reference 8

Figure 4.2
LABORATORY CATALYTIC OXIDATIVE COUPLING OF METHANE



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5 GASOLINE FROM NATURAL GAS USING THE ICI METHANOL AND MOBIL MTG PROCESSES

Mobil's fixed-bed MTG process, in combination with ICI low-pressure methanol synthesis, is the basis against which we compare the processes evaluated in this report. Although further development of the MTG process is under way, such as work on the fluidized-bed version of the reactor, we have chosen the original fixed-bed process for the base case design because it is the only version that has been proven in commercial operation.

Process Background

The conversion of methanol to gasoline has been made possible by Mobil's development of catalyst systems based on the company's proprietary synthetic zeolite, ZSM-5. This zeolite has unique pore channel sizes that are between those of Type A zeolites and faujasite (5-10 angstroms). These pore openings restrict passage of hydrocarbons to those having 9 to 10 carbon atoms, thus limiting the resulting products to the gasoline range. (The Fischer-Tropsch process catalyst, in contrast, is much less selective.) An added feature of the ZSM-5 zeolite, which allows it to operate at high temperatures without losing its activity and physical integrity, is its high ratio of silica to alumina. As a result, coke deposited during synthesis can later be burned off without damage to the zeolite.

The reaction mechanism can be represented by the following three steps:

(1) Methanol is first dehydrated to dimethylether (DME) over activated alumina catalyst.

(2) The DME then undergoes several reactions over the ZSM-5 catalyst; the first is the formation of light olefins (C_2-C_5).

(3) Those olefins, in turn, react further to form heavier olefins (C_5+), and are then rearranged into paraffins, cycloparaffins, and aromatics, via hydrogen transfer [1].

With long enough residence time in the reactor, the conversion of methanol is virtually complete, resulting in a high carbon yield [2]. Typical product yields from an MTG pilot plant operation are shown in Table 5.1. The C_5+ gasoline yield exceeds 80 wt% of the total hydrocarbon product.

Because the conversion of methanol to the hydrocarbon mixture is highly exothermic, the temperature rise is controlled by splitting the overall reaction between two reactors. Approximately 20% of the released heat is absorbed in the DME reactor, where a simple alumina catalyst is used; the adiabatic temperature rise in the zeolite reactor is controlled by the recycle of light gases. The reaction temperatures are kept in the 625°-780°F range.

The raw gasoline yield can be raised by blending C_4s (butanes and butenes) into the gasoline. An additional alkylation step can be used to further increase the gasoline yield by converting surplus C_3-C_4 hydrocarbons (mainly olefins) to higher molecular weight components. (In

this study we have not included an alkylation step because we judged that the additional capital investment cost was not justified for the small quantity of surplus C_3–C_4 olefins available—which are thus used as fuel in the process.)

Mobil states that the overall quality of gasoline obtained from the MTG process is at least equivalent to regular unleaded ([R+M]/2 = 88). Typical finished MTG gasoline properties are shown in Table 5.2.

Process Status

Initial catalyst studies at Mobil date back to the 1960s. Bench-scale work was started in the early 1970s in 5/8-in. and 1-1/4-in. internal diameter (ID) fixed-bed reactors. The larger of the bench-scale reactors contained 220 cm^3 of the ZSM-5 catalyst. Further work was carried out in a 4-b/d pilot plant that had a 4-in. ID reactor, packed with catalyst to a depth of 8 feet. This reactor allowed gas velocities that approached those proposed for the commercial design, and the bed depth was nearly 10 times that of the previous units. The results of the pilot plant work were similar to those obtained in the bench-scale work and formed the bases for the proposed commercial designs.

The first commercial project based on this technology, and still the only one that has been carried out, was begun in 1979 in New Zealand near Motunui, Tarankai, on the North Island. There, the government allocated 52.5 PJ*/y of Maui field natural gas for conversion to 570,000 metric tons per year (mt/y) gasoline (equivalent to 10.25 x 10^9 Btu/b gasoline) via the MTG process. Plant construction started in 1982, and the plant began operation in October 1985. At full design operation, the New Zealand plant can produce 14,450 b/d of gasoline from about 130 million scf/d of natural gas.

Mobil Oil managed plant construction, with Bechtel Petroleum, Inc., serving as the project services contractor. Hitachi-Zosen of Japan supplied a number of large fabricated plant assemblies. However, much of the rest of the construction was performed by local subcontractors. Davy McKee and Foster Wheeler participated with Bechtel as design contractors.

Project financing, of some US$1,200 million, was supplied by Citicorp. The original plant construction estimate was US$767 million in 1980. The reported estimated cost of the whole project in 1985 was US$1,475 million, including start-up costs, inflation, and interest during construction [4]. The plant is 75% owned by the New Zealand government and 25% by Mobil Oil.

The plant consists of two 2200-metric ton per day (mt/d) ICI methanol units feeding a two-stage conversion system. The first stage (which consists of a single, fixed bed adiabatic reactor) dehydrates a proportion of the methanol to DME as determined by the equilibrium. The second stage comprises five MTG reactors (all fixed bed) in parallel with four operating and one undergoing catalyst regeneration at any given time. The temperature is controlled by the injection of a large recycle stream (9 mols/mol makeup feed).

Further development of the process is expected to improve MTG economics as discussed below.

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* 1 PJ = 10^{15} joules.

Fluidized-Bed MTG Process

The advantages of a fluidized-bed reactor over the fixed-bed one are: better temperature control without a large recycle, improved yields and gasoline quality, continuous catalyst regeneration, lower pressure, and lower capital costs with a higher reactor throughput. Development work on the fluidized-bed version of the MTG reactor has been conducted concurrently with that on the fixed-bed one.

Early bench-scale tests on this reactor led to the construction of a 4-b/d pilot test facility in 1978. This pilot plant had a 4-in. ID internally baffled reactor and a regeneration system. Results of this pilot plant work substantiated some of the expected advantages of the fluidized-bed reactor: Gasoline yields were improved by about 3%, a higher octane number was achieved (97 versus 93 RON), and a much lower operating pressure was made possible (25 versus 300 psig). Typical yields from this pilot plant are shown in Table 5.3.

Mobil Research and Development Corp., Uhde GmbH, and Union Braunkohlen Kraftstoff AG, with financial support from the West German federal government and the U.S. Department of Energy (DOE), have built and operated a 100-b/d fluidized-bed MTG pilot plant near Bonn, West Germany. The results of pilot plant operation show that the process can be operated in a continuous mode with nearly total methanol conversion and low catalyst consumption. A definitive cost estimate of a commercial design of the fluidized-bed MTG process has not yet been published, however.

The 100-b/d pilot plant has been converted to test the methanol-to-olefins (MTO) process. Compared with the MTG process, the MTO process produces olefins (mainly C_3+), which can be converted to a liquid product by the Mobil Olefins-to-Gasoline and Distillate Process (MOGD). Like MTG, both MTO and MOGD are also based on Mobil's proprietary ZSM-5 catalyst systems.

A special feature of MOGD is its flexibility in allowing differing gasoline:distillate ratios of the product [6-10]. The gasoline is of high quality ([R+M]/2 = 89) and the distillate can be hydrotreated to furnish jet fuels and/or diesel fuels that are comparable to similar refinery products.

Other MTG Developments

Mobil Two-Stage Fischer-Tropsch/MTG Process

Mobil Research and Development Corp. has been testing a two-stage process consisting of Fischer-Tropsch (FT) and MTG catalysts for the production of gasoline from coal gasifier-generated syngases. Such a process could use an unbalanced syngas (in which the H_2:CO ratio is different from stoichiometric), thereby obviating the need to produce methanol. The second stage, the MTG reactor, would convert the FT product oxygenates and reform and crack paraffinic hydrocarbons. Because initial efforts to mix the two catalysts proved unsuccessful, all further work is being conducted in two separate FT and MTG reactors. With the addition of extra steam to the FT stage, an appreciable amount of syngas is shifted within the reactor without detriment to catalyst activity. Mobil expects that such a two-stage approach could prove to be more economical than the conventional MTG process. The development

program, which was partially funded by DOE, ended in December 1985. Although economic assessments of projected commercial designs were made, they were based on coal gasification, and the comparisons were made with the conventional Sasol-type FT process [11]. Thus, no published data are available to show that this approach is indeed more economical than the conventional MTG process for natural gas feeds.

The Haldor Topsoe Process

The Topsoe Integrated Gasoline Synthesis (TIGAS) process has been under development by Haldor Topsoe for several years, and a 1-mt/d gasoline pilot plant has been operating in Houston, Texas, since 1984. The TIGAS process integrates the operation of the syngas reformer, methanol production, and the MTG unit much more closely than did the original Mobil concept. All three units operate at approximately the same pressure to obviate the need for syngas compression before the methanol reactor. To achieve this integration, the operating conditions of the synthesis loop and of the methanol reactor had to be changed from those that are being used commercially.

The syngas reformer, the methanol loop, and the MTG reactor of the TIGAS process operate at a pressure of approximately 50 bar. Because a conventional reformer would give too high a methane slippage (i.e., unconverted methane in the dry reformer product) at this pressure, a two-step reforming sequence takes place in the TIGAS process, consisting of a primary reformer that operates on steam and a secondary reformer that operates on oxygen. An added advantage, in addition to higher pressure operation, of such a sequence is that a balanced syngas, without surplus hydrogen, is produced.

Operating the methanol synthesis reactor at lower pressures results in significant amounts of of other oxygenates besides methanol being produced. However, that is not a great disadvantage because the ZSM-5 catalyst in the MTG reactor can convert them to hydrocarbons.

The MTG bed operates at higher pressure than the approximately 20 bar that is used in the conventional Mobil process. The higher pressure could cause problems with durene formation and lead to automobile carburetor system problems. On the other hand, the higher than usual hydrogen content in the reactor reduces the production of olefins.

The 3-year test program on the TIGAS process will end in 1987, when design data will become available for a commercial plant [12].

Process Description

Figure 5.1 illustrates our process concept for the production of gasoline from natural gas. We set the base capacity at ~7,640 b/d raw gasoline. That corresponds to a methanol production capacity of 2,500 mt/d, which is similar to the largest single train plants in operation today. Although larger single train methanol plants (3,500–4,000 mt/d) are now considered possible by the design/contracting companies, none are either under construction or in planning. Table 5.4 shows the material balances, and Table 5.5 summarizes our main design bases. The stream flows in Table 5.4 group together all the C_5+ hydrocarbons that would constitute the gasoline product as a single component. Table 5.6 presents a detailed composition of the product slate from MTG synthesis on a water-free basis.

The process sequence consists of the following main sections:

- Natural gas steam reforming and steam generation
- Crude methanol synthesis
- MTG synthesis and purification.

We have assumed that sufficient high-pressure (HP) steam is raised in the reforming section furnace to meet the needs of the large turbine-driven compressors and to generate all the electricity required by both battery limits process plant and offsites. Figure 5.2 shows the steam balances. Most of the HP steam is consumed in condensing turbines, but some of it is exhausted as medium-pressure (MP) steam to provide reformer feed and process and offsites thermal energy. Thus, the whole plant is self-sufficient in regard to its utilities (steam, electricity, deaerated water), with the natural gas reformer feed constituting the only input. Adequate energy is available in the by-product streams to eliminate the need for natural gas as fuel during steady operation. The steam reforming furnace includes auxiliary firing for steam generation when natural gas is used as fuel only during start-up. The crude methanol synthesis section differs from a standard methanol plant in that no distillation facilities are included for methanol purification. Crude methanol (the composition is shown in Table 5.4, stream 18) is fed directly to the MTG section.

The main energy aspects of our process design concept are shown in Table 5.7. The overall energy efficiency of 50.2% is somewhat lower than the 53% [14] quoted for the New Zealand plant primarily because of the use of surplus liquefied petroleum gas (LPG) for furnace fuel.

Natural Gas Reforming and Steam Generation

Natural gas feed is desulfurized in activated carbon adsorbers and preheated to 190°F. It is then passed countercurrently through a water saturator column against water entering at 400°F to raise the gas temperature to 390°F and to transfer 50% of the water needed in the reformer feed. The balance of the steam is obtained from the methanol recycle compressor turbine exhaust. The total reformer feed is heated to 1000°F in a convection coil within the flue duct of the reformer furnace. The reaction is carried out in the radiant section of the furnace. The exit temperature of the crude reformer product is 1600°F, and the pressure is 295 psia.

The fuel for the reformer furnace is provided by various purge streams as detailed in Table 5.7. (Natural gas firing is used only during start-up.) The hot flue gas leaving the radiant section pass through convection tube banks that superheat steam, preheat reformer feed, and preheat combustion air.

The reformer product, which is at 1600°F, is cooled in stages to 180°F, with heat recovered for use in the generation of steam, including boiler feed water deaeration. Final cooling to 100°F (38°C) is against cooling water.

Methanol Synthesis

The cooled syngas from reforming heat recovery is compressed to 1500 psia in a two-casing centrifugal compressor with an intercooler. It is fed to the methanol synthesis reactor along with a recycle stream, which is compressed in a single casing machine. A high ratio of recycle:feed is maintained (-5.3:1, molar) for temperature control. The temperature at the reactor exit is 520°F.

The methanol reactor stream is cooled to 180°F, with heat recovery, and finally to 100°F against cooling water. The recovered heat is used in preheating feed streams and in the steam generation system. The cooled reactor methanol product at 100°F goes through a stabilization vessel that separates the condensed liquid from the vapor. Most of the methanol, DME, higher alcohols, and water in the crude product are present in the liquid phase, which constitutes the crude methanol feed (the composition is shown in Table 5.5) to the MTG section. A major proportion of the vapor phase is recycled to the methanol reactor, and a small purge is taken (and used as reformer fuel) to prevent the buildup of inerts. Both the purge vapor phase and the condensed liquid phase pass through turbines to recover energy (as detailed in Table 5.7) to be used in the generation of electricity.

Both compressors in methanol synthesis are driven by steam turbines. The syngas compressor uses a condensing turbine that exhausts at 1.27 psia. The recycle compressor is driven by a noncondensing back-pressure turbine that exhausts steam at 350 psia and 510°F for use in the reformer feed.

MTG Synthesis and Purification

Crude methanol is fed from storage to the DME reactor after preheating to approximately 600°F by heat exchange with the MTG reactor product gases. A single reactor, packed with activated alumina catalyst, is used. Methanol is partially dehydrated at about 350 psia in the fixed-bed DME reactor. The product gases, leaving the DME reactor at 770°F and consisting of DME, methanol, and water, are then fed to the MTG reactors. Four fixed-bed MTG reactors are used in the design; at any one time, three reactors are on-stream, and one reactor is undergoing regeneration. Each reactor is assumed to be packed with Mobil's ZSM-5 catalyst. The temperature rise from the exothermic reactions in the MTG reactors is controlled by recycling cooled product offgases. A recycle gas:DME reactor feed gas ratio of 9:1 (molar) is used for that purpose. The MTG reactor product gases are cooled to 200°F with the heat recovered used to preheat MTG reactor feed streams and to generate steam. Final cooling to 130°F takes place in an air cooler where most of the C_5+ components and water have been condensed. The vapor phase is recycled to the MTG reactor after a purge is taken for use as reformer fuel. The liquid phase is fractionated to remove light ends overhead and raw gasoline as the bottoms stream. The light ends are also used as fuel in the reformer furnace. The separation criterion for the column is to reduce the C_4 (butanes/butenes) level in the gasoline to <3 wt%. The Reid vapor pressure of the raw gasoline is close to that indicated by Mobil (see Table 5.2), which is 9.0.

Process Discussion

Our process concept is essentially derived from earlier SRI work for the steam reforming and methanol synthesis sections (Process Economics Program--PEP--Report 148, Part II, *Costs of Synthesis Gases and Methanol*, February 1983) and published data for the MTG process. As such, the concept is not completely optimized. For instance, steam reforming pressures, which are kept relatively low (295 psia at exit), are typical of the ICI high-energy efficiency process and are aimed at maximizing the methane conversion. The higher pressures (-440 psia) used in the New Zealand facility have required more purge from MeOH synthesis (owing to the higher methane slippage) but have the advantage of reducing syngas compression costs.

We have used steam turbine drives for all the large compressors (as shown in Figure 5.2) and electric drives for the smaller machines in the 1500-10,00 bhp range (e.g., the air blower, flue gas extractor, cooling water pumps, and boiler feedwater pumps). Doing so would save on capital costs--an approach we consider to be justified for remote locations where natural gas energy would be relatively cheap and capital costs significantly higher than U.S. Gulf Coast or other developed locations.

We have followed this guideline in other design aspects such as thermal energy recovery and MTG gasoline purification. A less rigorous thermal recovery, as adopted in our design concept for the ICI methanol process (PEP Report 148, Part II), would result in substantial savings in capital costs.

We have assumed a simple gasoline recovery/purification system that comprises a partial condensation step followed by fractionation to separate light ends. The New Zealand plant also includes an absorption column to recover C_5+ components from MTG purge gas by scrubbing with gasoline and a gasoline fractionator to split the raw gasoline into a lighter and a heavier product. These components allow the possible high durene level to be dealt with in the hydrotreatment of heavy gasoline. In our process concept a single liquid product is made; although the data used (Table 5.6) indicate a durene level of 4 wt%, we have assumed that that level does not lower the product's value as a high quality gasoline. We believe a single product would produce savings in storage and transportation costs.

As shown in our stream flows, significant levels of C_3 and C_4 components are rejected in the MTG purge and light ends (streams 22 and 25) for use as fuel. We considered the possibility of their recovery for LPG sales or for use in alkylate synthesis to blend into the raw gasoline, but we judged that the scale of such operations would be too small to be cost-effective.

Cost Estimates

Table 5.8 breaks down capital investment costs for a U.S. Gulf Coast location and for a PEP Cost Index (an SRI proprietary multiclient program) of 445 (mid-1986). The data are derived from previous SRI estimates and from information provided by industry contacts. The total fixed investment of $423 million is approximately distributed as follows:

	Percent
Steam reforming and methanol synthesis	40.4
MTG (gasoline synthesis and purification)	25.2
Offsites	34.4
	100.0

Our estimates of the capital estimate relate well to the original 1980 estimate for the New Zealand facilities, which was US$767 million for the conversion of methanol from two trains, each with 2200 mt/d capacity (compared with a single train of 2500 mt/d capacity in our evaluation). As stated before, the final cost for the New Zealand project in 1985 was US$1,475 million (the cumulative cost of the project in dollars of the day). The cost escalation was mainly due to inflation and interest (capitalized) during the construction period.

To provide a reference basis against which the costs in various remote locations may be determined, Table 5.9 presents the production costs in 1986 dollars for a U.S. Gulf Coast location.

Although we commonly use 10%/y of total fixed capital (TFC) for depreciation (straight line basis, 10 year plant life) and 25%/y of TFC for return on investment (ROI) before taxes, which would represent a total of 35%/y of TFC for capital-related charges, the required rate would depend on many factors. They would include:

- Project financing leverage (loan/equity ratio)
- Interest rates on the loan
- Minimum acceptable rate on equity (to take account for dividends to stockholders and the risk element)
- Operational life of the plant.

We estimate that a minimum of 20%/y on TFC over the plant life would be more appropriate for large investments in remote locations--for which the financing is assumed to be largely by loan and the plant life generally longer than the standard 10 years. This estimate is valid if we assume that loan interest rates would be less than 10%/y (as applied in 1986). Accordingly, our production costs in Table 5.9 show a total of 20%/y on TFC for capital related charges.

The full cost may be expressed by the following equation:

$$F_{MTG} = 10.31N + 4.483f_M + 2.38f_L + 6.26f_A + 33.56f_C \ , \qquad (5.1)$$

where, F_{MTG} is full cost in 1986 US$/b, including 20%/y of TFC for capital related costs. f_M, f_L, f_A, and f_C are location factors for costs relating to raw materials, labor, additional cash costs, and capital, respectively (all are = 1 for the U.S. Gulf Coast). N is value of natural gas ($/$10^6$ Btu).

Equation 5.1 is convenient because it shows the relative contributions of the individual cost elements to which appropriate location factors can be applied to determine the full cost. As an illustration, taking natural gas at zero value, the capital location factor (f_C) at 1.5 and all other

location factors at 1.2, the full cost (F) is $66.09/b of gasoline. The corresponding U.S. Gulf Coast cost would be $69.96/b when natural gas is $2.30/$10^6$ Btu (the current average U.S. price). Thus, for the assumed location factors the process would offer no advantage over U.S. Gulf Coast costs when due allowance is made for transportation costs.

If an overall cost location factor f_o can be applied to all cost elements, equation 5.1 can be simplified to:

$$F_{MTG} = 10.31N + 46.68f_o \qquad (5.2)$$

Figure 5.3 illustrates the dependence of gasoline costs on natural gas values for various levels of the overall cost location factor. Table 5.10 shows the direct cash costs by section.

Table 5.1

TYPICAL PRODUCT YIELDS FROM THE MTG PILOT PLANT
(Barrels per Day)

Product, wt%	
Hydrocarbons	36.48
Water	63.49
CO, CO_2	0.03
Methanol	0.00
DME	0.00
Total	100.00
Hydrocarbon product, wt%	
Methane and ethane	1.56
Ethylene	0.04
Propane	5.60
Propylene	0.20
n–Butane	2.90
i–Butane	8.70
Butenes	0.90
C_5+ gasoline	80.10
Total	100.00
Aromatics, wt% of total	29.60

Source: Reference 3.

Table 5.2

FINISHED MTG GASOLINE PROPERTIES

Components, wt%	
Butanes	3
Alkylate	3
C_5+ gasoline	94
Total	100
Composition, vol%	
Paraffins	53
Olefins	12
Naphthenes	7
Aromatics	28
Total	100
Physical Properties	
Research octane	
Clear	93
Leaded, 3 cm^3 TEL/USG	101
Motor octane	
Clear	83
Leaded, 3 cm^3 TEL/USG	90
Reid vapor pressure, psig	9.0
Specific gravity	0.728
Sulfur, wt%	Nil
Nitrogen, wt%	Nil
Corrosion, copper strip	1A
ASTM distillation, °F	
10%	114
30%	145
50%	198
90%	330

Source: Reference 3.

Table 5.3

YIELDS FROM METHANOL IN A PILOT PLANT FLUIDIZED-BED MTG REACTOR

Average bed temperature, °F	775
Pressure, psig	25
Weight hourly space velocity	1.0
Yields, wt% of methanol charge	
Methanol + ether	0.2
Hydrocarbons	43.5
Water	56.0
CO, CO_2	0.1
Coke, other	0.2
Total	100.0
Hydrocarbon product, wt%	
Light gas	5.6
Propane	5.9
Propylene	5.0
i-Butane	14.5
n-Butane	1.7
Butenes	7.3
C_5+ gasoline	60.0
Total	100.0
Gasoline (including alkylate)	88.0
LPG	6.4
Fuel gas	5.6
Total	100.0

Source: Reference 5.

Table 5.4
GASOLINE FROM NATURAL GAS USING THE ICI METHANOL AND MOBIL MTG PROCESSES: STREAM FLOWS

Plant Capacity: **7,640 b/sd gasoline or 2.51 x 10^6 b/y (equivalent to ~295,000 mt/y) at a 0.90 stream factor**

Stream Flows

	Molecular Weight	(1) Total Natural Gas Feed	(2) Sweetened Feed	(3) Natural Gas Fuel	(4) Reformer Steam	(5) Reformer Feed	(6) Reformer Product	(7) Process Water	(8) Steam From Reformer	(9) Saturated Reformer Feed
Methane	16.04	124,507.94	122,472.97	2,034.94		122,472.97	19,583.41			122,472.97
Carbon dioxide	44.01	1,968.61	1,936.44	32.17		1,936.44	113,278.09			1,936.44
Carbon monoxide	28.01						137,740.20			0.00
Hydrogen	2.02						48,735.31			0.00
Nitrogen + Inerts	28.01	1,794.16	1,764.84	29.32		1,764.84	1,764.84			1,764.84
Ethane	30.07	6,633.64	6,525.22	108.42		6,525.22				6,525.22
C_3+	69.13	8,433.36	8,295.53	137.83		8,295.53				8,295.53
Water	18.02				229,012.08	458,008.67	278,264.58	2,321,454	725,349.00	228,996.59
Oxygen	32.00									
Methanol	32.04									
Dimethyl ether	46.07									
Higher alcohols	46.07									
Total (lb/h)		143,338	140,995	2,343	229,012	599,004	599,366	2,321,454	725,349	369,992
Total (kg/h)		65,017	63,954	1,063	103,878	271,704	271,868	1,055,206	329,704	167,826
Total (lb-mol/h)		8,212.25	8,078.03	134.22	12,712.06	33,501.29	48,396.00	128,826.53	40,252.46	20,789.23

Stream Flows

	Molecular Weight	(10) Condensate	(11) Compressed Syngas Feed	(12) Recycle Gas	(13) Cold Feed	(14) Hot Feed	(15) Methanol Reactor Product	(16) Purge Gas Scrub Water	(17) Methanol Synthesis Purge	(18) Crude Methanol to Synthesis
Methane	16.04		19,583.41	388,146.83	224,251.56	183,476.52	407,730.24		19,583.41	
Carbon dioxide	44.01		113,278.09	113,387.68	124,666.11	101,999.66	119,108.09		5,720.41	
Carbon monoxide	28.01		137,740.20	80,813.52	120,204.47	98,349.24	84,890.73		4,077.22	
Hydrogen	2.02		48,735.31	291,655.98	187,215.21	153,176.08	306,371.17		14,715.17	
Nitrogen + Inerts	28.01		1,764.84	34,980.61	20,209.99	16,535.47	36,745.46		1,764.84	
Ethane	30.07						0.00			
C_3+	69.13						0.00			
Water	18.02	278,194.14	58.01	576.49	348.96	285.54	44,826.85	8,016.83	818.62	51,448.57
Oxygen	32.00						0.00			
Methanol	32.04			15,864.21	8,725.47	7,139.05	246,493.44		800.42	229,829.14
Dimethyl ether	46.07						147.42			147.42
Higher alcohols	46.07						271.80			271.80
Total (lb/h)		278,194	321,160	925,425	685,622	560,964	1,246,585	8,017	47,480	281,697
Total (kg/h)		126,187	145,676	419,766	310,993	254,449	565,442	3,636	21,537	127,776
Total (lb-mol/h)		15,3442.07	32,953.24	176,106.37	114,982.78	94,076.83	194,627.99	445.00	8,929.06	10,037.57

Stream Flows

	Molecular Weight	(19) DME reactor Effluent	(20) MTG reactor Effluent	(21) Recycle Stream	(22) Phase Separation Purge	(23) Phase Separation Product	(24) Water from Phase Separation	(25) Light ends Overhead	(26) Gasoline Product
Hydrogen	2.02		29,807.26	29,756.45	50.68	0.13		0.13	
Carbon dioxide	44.01		978,582.13	976,916.83	1,663.72	1.58		1.58	
Carbon monoxide	28.01		103,837.84	103,661.19	176.54	0.11		0.11	
Methane	16.04		597,231.69	596,214.19	1,015.37	2.14		2.14	
Ethylene	28.01		2,222.74	2,202.59	3.75	16.40		16.40	
Ethane	30.07		38,671.02	38,207.60	65.07	398.35		398.35	
Propylene	42.08		9,492.50	9,280.94	15.81	195.75		195.74	0.02
Propane	44.10		227,328.81	221,828.24	377.78	5,122.79		5,122.28	0.51
i-Butane	58.12		176,701.56	167,967.13	286.05	8,448.37		7,772.50	675.87
Butenes	56.11		19,523.23	18,415.06	31.36	1,076.81		872.22	204.59
n-Butane	58.12		49,395.78	46,161.92	78.61	3,155.24		1,564.90	1,590.33
C_5+	95.68		189,834.14	109,672.86	186.78	79,974.50		12.00	79,962.50
Water	18.02	100,887.84	192,983.32	13,630.06	23.21	44.30	179,285.74	44.30	
Methanol	32.04	53,962.56							
Dimethyl ether	46.07	126,846.73							
Higher alcohols	46.07								
Total (lb/h)		281,697	2,615,612	2,333,915	3,975	98,436	179,286	16,003	82,434
Total (kg/h)		127,776	1,186,423	1,058,647	1,803	44,650	81,323	7,259	37,391
Total (lb-mol/h)		10,037.57	101,636.32	90,337.60	153.85	1,192.04	9,061.84	313.65	878.39

Table 5.5

GASOLINE FROM NATURAL GAS USING THE ICI METHANOL AND MOBIL MTG PROCESSES: DESIGN BASES

Steam reforming section	
Temperature	
Inlet	1000°F
Exit	1600°F
Pressure (psia)	
Inlet	320
Exit	295
Steam/carbon molar ratio	~3.0:1.0
Methane conversion (%)	84 (corresponds to 20°F approach to equilibrium)
Catalyst	Ni-based catalyst (3760 ft^3) such as ICI 574
Methanol synthesis section	
Temperature	
Inlet	470°F
Exit	520°F
Pressure (psia)	
Inlet	1500
Exit	1350 at section exit
Catalyst	Cu-based catalyst (9600 ft^3)
Carbon efficiency (%)	96 based on CO + CO_2 in makeup syngas
Feed:recycle molar ratio	1.0:5.34
Crude methanol composition (wt%)	
Methanol	74.5
Higher alcohols	8.8
DME	<0.1
Water	16.7
MTG section	
DME reactor	
Temperature	
Inlet	600°F
Exit	770°F
Pressure (psia)	
Inlet	~350
Exit	315
DME:methanol molar ratio in product	1.58:1
Catalyst	Alumina (58,000 lb)
MGT reactors	
Temperature	
Inlet	650°F
Exit	780°F
Pressure (psia)	
Inlet	315
Exit	300
Catalyst	Mobil's ZSM-5 (total 223,000 lb)
Conversion/yields	As shown in Table 5.6
Feed:recycle molar ratio	1:9

Table 5.6

GASOLINE FROM NATURAL GAS USING THE ICI METHANOL AND MOBIL MTG PROCESSES: GASOLINE SYNTHESIS REACTOR PRODUCT SLATE*

Plant Capacity: **7,640 b/sd gasoline or 2.51 million b/y (equivalent to ~295,000 mt/y) at 0.90 stream factor**

	Molecular Weight	Pounds per Hour	Mass %
Methane	16.04	1,018	0.994
Ethane	30.07	463	0.453
Ethylene	28.05	20	0.020
Propane	44.10	5,501	5.375
Propylene	42.08	212	0.207
n-Butane	58.12	3,234	3.160
i-Butane	58.12	8,734	8.534
Butenes	56.11	1,108	1.083
n-Pentane	72.15	1,602	1.565
i-Pentane	72.15	11,203	10.946
Pentenes	70.14	2,216	2.166
Cyclopentane	70.14	322	0.315
C_8-cyclics	84.16	1,541	1.506
3-Methylpentane	86.18	4,654	4.548
i-Hexane	86.18	11,666	11.399
Hexenes	84.16	1,632	1.595
n-Heptane	100.21	212	0.207
i-Heptane	100.21	504	0.492
C_7-olefins	98.19	1,995	1.949
Other heptanes	100.21	1,834	1.792
n-Octane	114.23	50	0.049
Other octanes	114.23	6,981	6.822
n-Nonane	128.26	141	0.138
Branced decanes	142.29	836	0.817
Benzene	78.11	212	0.207
Toluene	92.14	2,126	2.077
Ethylbenzene	106.17	635	0.620
(p&m)-Xylene	106.17	7,072	6.910
o-Xylene	106.17	1,995	1.949
Trimethylbenzenes	120.20	7,284	7.117
Methyl-ethyl-benzenes	120.20	2,851	2.786
C_3-alkylbenzenes	120.20	161	0.157
Durene	134.22	3,335	3.258
C_{10}-alkylbenzenes	132.22	1,964	1.920
C_{11}-alkylbenzenes	142.20	615	0.600
Heavies	56.23	1,189	1.162
CO_2	44.01	1,665	1.627
CO	28.01	177	0.173
H_2	2.02	51	0.050
Total (water-free basis)		102,344	100.000
H_2O product	18.02	128,069	
Total product		230,412	

Basis: Methanol equivalent flowrate of 7,190.85 lb-mol/h (230,412 lb/h).
* Excludes water or light gas recycle in feed.
Source: Reference 13.

Table 5.7

GASOLINE FROM NATURAL GAS USING THE ICI METHANOL AND MOBIL MTG PROCESSES: MAIN ENERGY-RELATED FEATURES OF THE SRI DESIGN CONCEPT

Process Aspect	Main Quantitative Data	10^6 Btu/h
Overall energy efficiency	Natural gas feed	3247
	Natural gas fuel*	35
	Total (higher heating value--HHV-basis)	3282
	Raw gasoline (HHV basis)	1648
	Energy efficiency	50.2%
Reformer furnace fuel	Methanol synthesis purge	1368
	MTG synthesis purge	50
	Light ends	325
	Total (HHV basis)	1743
Distribution of reformer thermal output	Feed preheat and endotherm	1075
	Steam generation	279
	Air preheat	128
	Losses	261
	Total (HHV basis)	1743
Energy for HP steam	Total required	1125
	Source:	
	Reformer furnace	279
	By heat recovery	
	From reforming	618
	From methanol synthesis	128
	From MTG synthesis	100
	Total	1125
Electricity requirements	Steam reforming	9220
	Methanol synthesis†	-5831
	MTG synthesis	2330
	Offsites miscellaneous	1000
	Total	6719

* Natural gas firing is required only during start-up.

† From power recovery in the depressurization of methanol purge gas and crude methanol product.

Table 5.8

GASOLINE FROM NATURAL GAS USING THE ICI METHANOL AND MOBIL MTG PROCESSES: CAPITAL INVESTMENT

Plant capacity: 7,640 b/sd of gasoline or 2.51 million b/y (equivalent to ~295,000 mt/y) at 0.9 stream factor
PEP Cost Index = 445; U.S. Gulf Coast location

	Millions of Dollars
Battery limits	
Steam reforming	94
Methanol synthesis	76
MTG (gasoline synthesis and purification)	106
Total battery limits	276
Offsites	
Waste treatment and utilities (power generation, cooling water, demineralized water, compressed air, etc.)	44
General service facilities	75
Tankage	26
Total offsites	145
Total fixed capital	421

Table 5.9
GASOLINE FROM NATURAL GAS USING THE ICI METHANOL AND MOBIL MTG PROCESSES: PRODUCTION COSTS

Plant capacity: 7,640 b/sd of gasoline or 2.51 million b/y (equivalent to ~295,000 mt/y) at a 0.9 stream factor
PEP Cost Index = 445; U.S. Gulf Coast location

	Millions of Dollars	
Capital investment		
Battery limits	276	
Offsites	145	
Total fixed capital (TFC)	421	
	Cents per Pound	**Dollars per Barrel**
Raw materials and utilities		
Natural gas, $N*/10^6 Btu	3.983N	10.31N
Reforming catalyst, $3.88/lb	0.07	0.169
Methanol synthesis catalyst, $5.47/lb	0.32	0.816
DME catalyst, $5/lb	0.05	0.116
MTG catalyst, $15/lb	0.51	1.333
Maintenance materials, 1.5%/y of BL cost	0.64	1.650
Operating materials, miscellaneous	0.15	0.399
Utilities	nil	nil
Variable cost	3.983N+1.73	10.31N+4.483
Labor		
Operating labor, 8 men/shift, $21.82/man-hour	0.23	0.608
Maintenance labor, 1.5%/y of BL cost	0.64	0.650
Control laboratory, 20% of operating labor	0.05	0.122
Total labor	0.92	2.380
Additional cash costs		
Plant overhead, 80% of total labor	0.74	1.904
Taxes and insurance, 2%/y of TFC	1.30	3.356
G&A, sales, research	0.38	1.000
Total cash costs	3.983N+5.07	10.31N+13.123
Capital related costs (CRC), 20%/y of TFC	12.96	33.555
Total cost (including CRC)	3.983N+18.03	10.31N+46.678

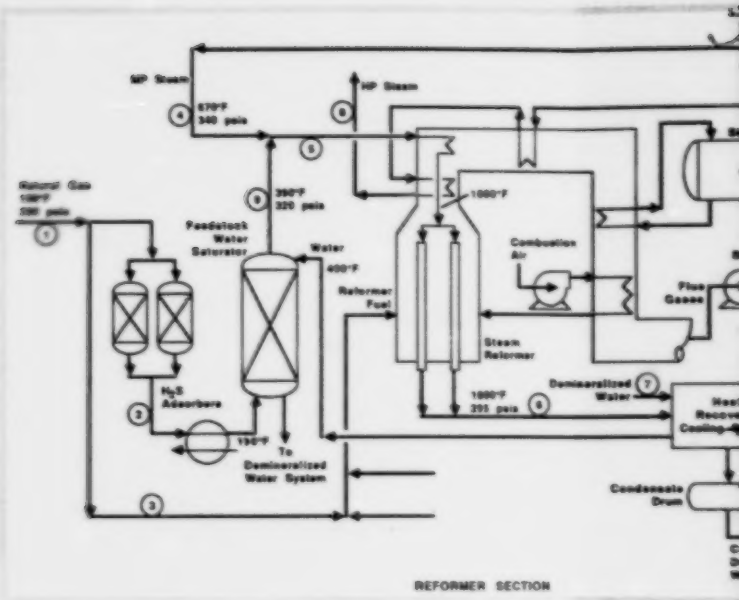
*N = value of natural gas.

Table 5.10

GASOLINE FROM NATURAL GAS USING THE ICI METHANOL AND MOBIL MTG PROCESSES: CASH COSTS BY SECTION
(Thousand of U.S. Dollars per Year)

Plant capacity: 7,640 b/d of gasoline or 2.51 million b/y (equivalent to ~295,000 mt/y) at a 0.9 stream factor
PEP Cost Index = 445; U.S. Gulf Coast location

	Section			
	Steam Reforming (Including steam generation)	Methanol Synthesis	MTG (Gasoline synthesis)	All 3 Sections
Materials and utilities				
Natural gas, at $N/10⁶ Btu	—	—	—	25,875N
Catalysts	424	2,048	3,637	6,109
Maintenance materials	1,673	1,044	1,425	4,142
Operating materials, miscellaneous	376	250	376	1,002
Labor				
Operating	572	381	572	1,525
Maintenance	1,673	1,044	1,425	4,142
Control laboratory	114	76	114	304
Additional cash costs				
Plant overhead	1,887	1,201	1,689	4,777
Taxes and insurance	3,403	2,139	2,897	8,439
G&A, sales, research	—	—	—	2,510
Total Cash Costs	10,122	8,183	12,135	32,950 + 25,875N



REFORMER SECTION

Figure 5.1
GASOLINE FROM NATURAL GAS USING ICI METHANOL PROCESS AND MOBIL MTG PROCESS

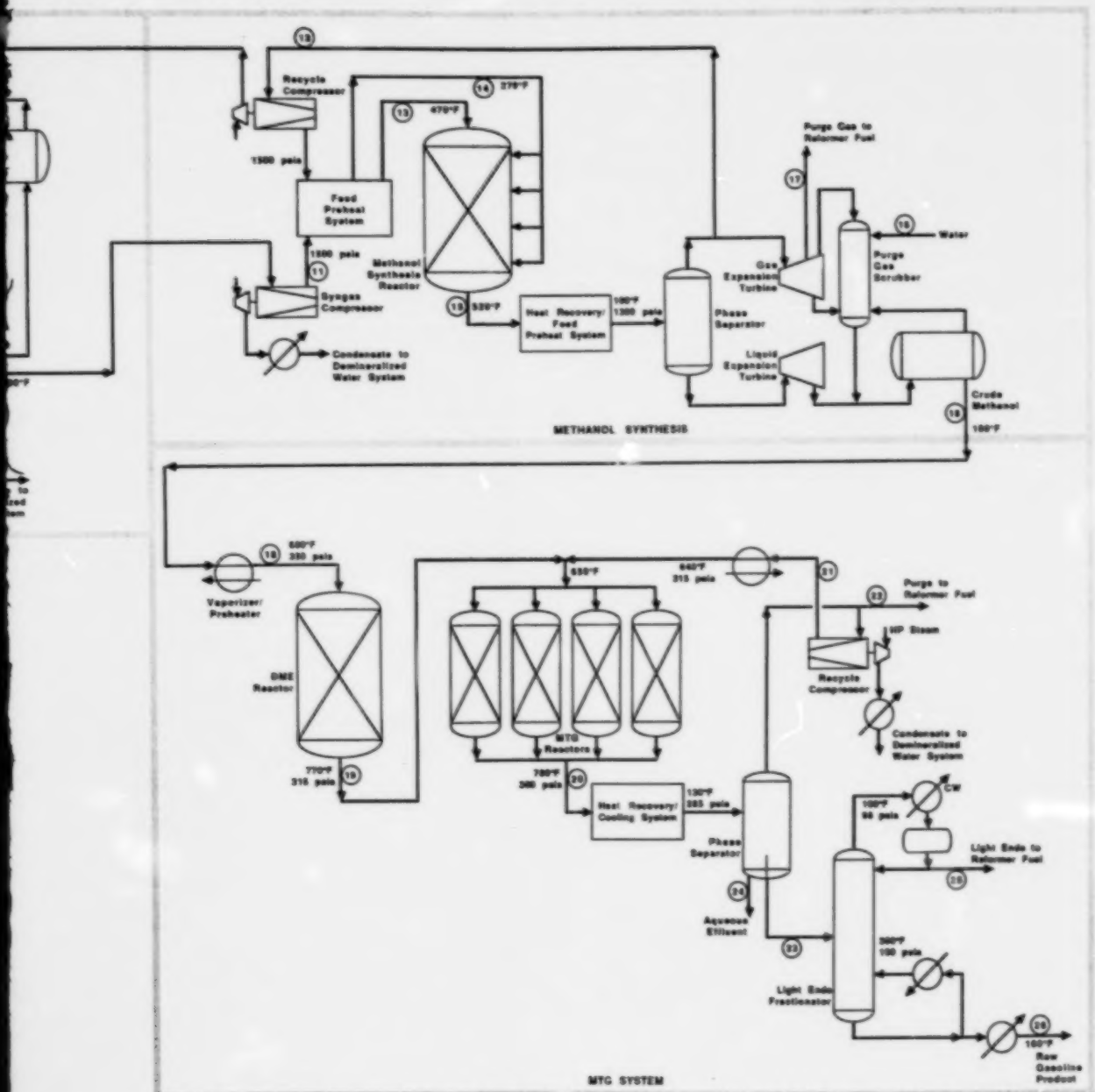


Figure 5.2

GASOLINE FROM NATURAL GAS: STEAM BALANCES

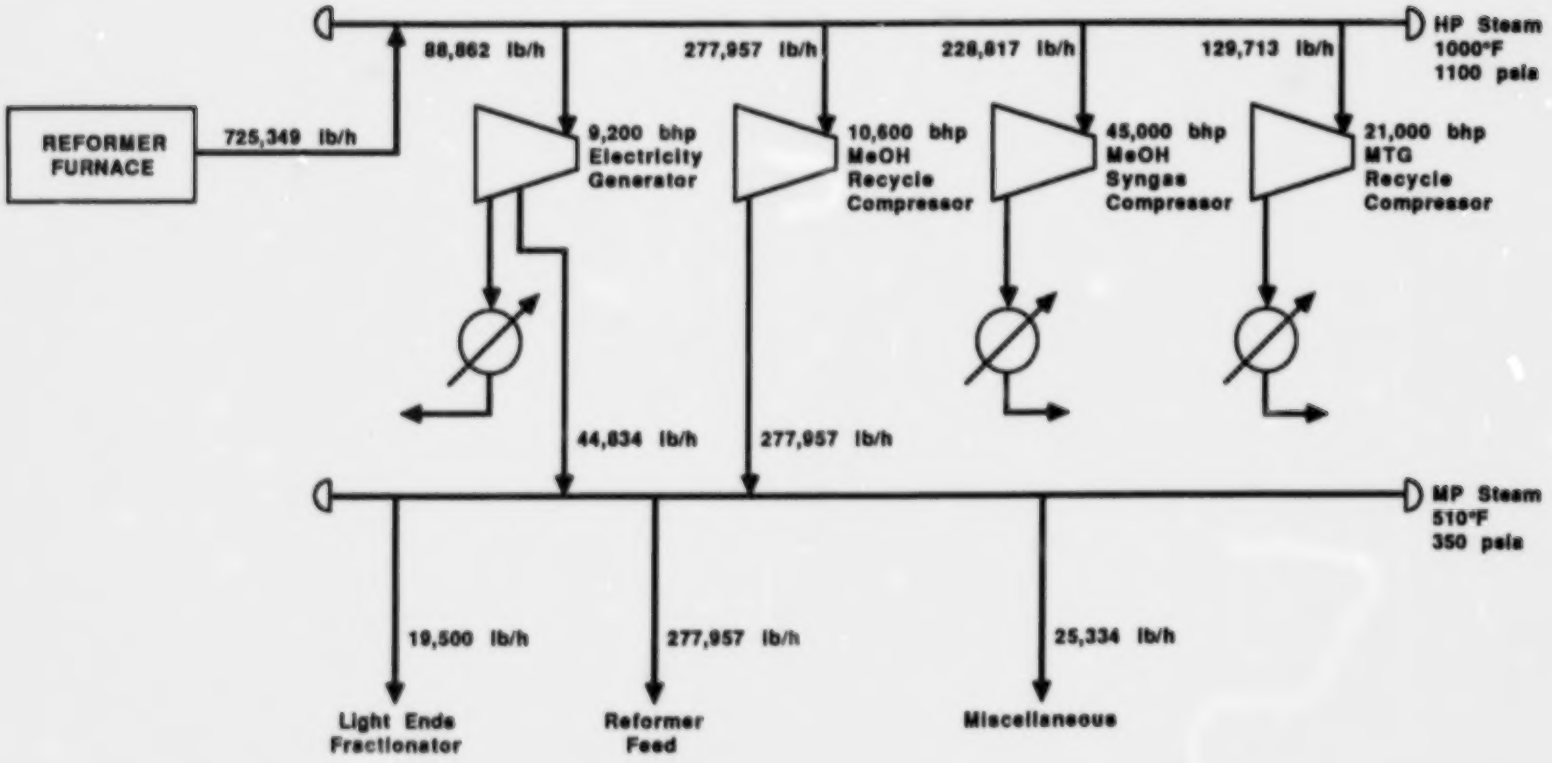
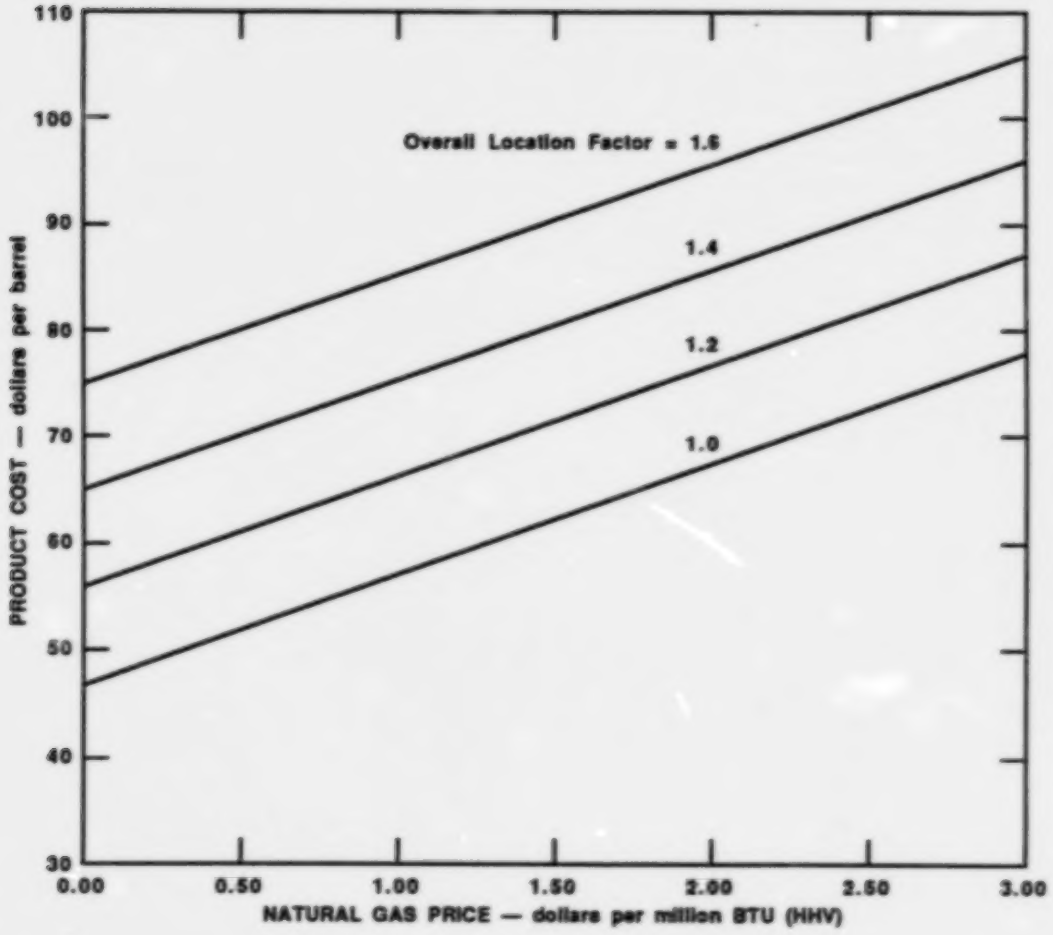


Figure 5.3

GASOLINE FROM NATURAL GAS USING THE ICI METHANOL AND MOBIL MTG PROCESSES: PRODUCT COSTS AS A FUNCTION OF NATURAL GAS PRICE AND LOCATION FACTOR



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6 GASOLINE FROM NATURAL GAS USING ARCO'S METHANE OXIDATIVE COUPLING AND OLEFIN OLIGOMERIZATION CONCEPTS

As discussed in Section 2, many companies continue to actively research the direct conversion of methane to useful products (without going through a syngas step). Among various possibilities, the oxidative coupling of methane offers the prospect of furnishing a hydrocarbon mixture that is mainly olefinic in nature and that contains a large proportion of ethylene and propylene. Such a mixture may be converted to a gasoline/distillate product by an oligomerization step; the ethylene and propylene it contains can be used to manufacture polymers and/or petrochemicals. In this section, we evaluate the economics of two possible processes for gasoline/distillate production that are based on ARCO's concepts for both the oxidative and the oligomerization steps. The essential difference in the two processes is the type of reactor system that we have assumed for the oxidative coupling step.

ARCO has patented a series of promoted metal oxide catalyst systems; the preferred one is based on manganese (Mn) on a silica (SiO_2) support [1]. ARCO has described two reactor configurations:

- A fluidized-bed/Redox system
- An air or oxygen Cofeed system.

The same Mn based type of catalysts can be used for both systems. In the fluidized-bed/Redox system, the catalyst is the oxygen carrier or donor. As in fluidized catalytic cracking (FCC), the catalyst is regenerated (by reoxidation with air) in a zone that is separate from that for methane conversion. Any coke that is deposited on the catalyst as CO_2 is also removed in the regeneration zone. The Cofeed system entails cofeeding air or oxygen to the reactor. Thus, while the Redox system requires a more complex reactor design than does the Cofeed system, it does not need an air separation system to provide oxygen or expensive separation of nitrogen from unconverted methane if air is used in the feed.

In addition, the Redox system has the desirable heat transfer characteristics of FCC systems that allow it to operate in thermal balance. The incoming natural gas, recycle, and air feed streams can be set at relatively low temperatures. Under these conditions, the exit temperatures of the regeneration offgas and product streams are determined by the reaction exotherm, which can be controlled by the catalyst circulation rate and the recycle level.

A different approach is necessary to control the temperature of a Cofeed reactor. A tube and shell type of reactor cannot be used because no coolants are satisfactory for the high temperatures used (~1500°F) for this duty. (Inorganic molten salts such as $NaNO_2/NaNO_3/KNO_3$ mixtures are stable only to 850°F--other higher temperature systems based on Na-K alloys or mercury must be ruled out because of their obvious hazards and high costs.) Possible reactor types that can be used for the Cofeed system include:

- A single fixed-bed vessel with "cold shot" at several levels of the catalyst bed

- A multibed vessel with intercooling and staged oxygen feed
- A single fixed-bed adiabatic reactor in which the temperature rise is limited by the addition of a large recycle and/or an inert diluent such as steam.

In our evaluation of the Cofeed system, we have assumed a multibed reactor with intercooling and staged oxygen feed.

For both processes evaluated in this section, we have used material balance/stream flow data provided by ARCO. Although the oxidative coupling data are strictly for the Redox case, ARCO suggested that the same basic yield slate would also apply to the Cofeed case. These data are shown in Table 6.1.

Currently, no commercially established process is available to convert the C_2+ hydrocarbon mixture that is obtained by the ARCO route (as shown in Table 6.1). Mobil's olefin to gasoline and distillate (MOGD) process, which is based on ZSM-5 type zeolite catalysts, has been tested on refinery scale equipment [2] and is primarily effective with a C_3+ olefins feedstock. Table 6.2 shows that ethylene is more difficult to oligomerize than propylene and higher olefins. ARCO's research indicates that an ethylene-rich olefinic feedstock can be converted to liquid hydrocarbons in the presence of ZSM-5 zeolites and crystalline borosilicate molecular sieve catalysts by the use of short contact times and high severity conditions [3]. Although the development of ARCO's oligomerization concept is somewhat less advanced than its oxidative coupling concept, we have assumed that the technical targets represented by the company's stream flow data can be achieved.

Process Description

Redox Case

Figure 6.1 is a flow diagram of our process concept. The plant capacity is 8,060 b/sd of gasoline/distillate and corresponds to a natural gas feed rate of about 86 million scf/d. We have set the base capacity for a single-train FCC type reactor/regenerator for the Redox case. Preliminary design and cost data were provided by Air Products (Houdry Division). Table 6.3 shows the stream flows, which are based on data provided by ARCO.

Natural gas is desulfurized on active carbon adsorption beds and fed along with a recycle stream to a fluidized-bed reactor similar in basic design to that used for FCC. The reactor feed inlet temperature is 110°F, and the crude product leaves at 1470°F. In the regeneration zone the catalyst is reoxidized with air. Any coke deposited on the catalyst is simultaneously burned off and removed as CO_2 gas in the regeneration exit gas, which leaves at 1475°F. The inlet operating pressure of the reactor is 65 psia. A multistage, single-casing centrifugal compressor is used for the air feed. The heat of reaction is absorbed in heating the reactant mixture and the air feed to the regeneration zone.

The crude Redox product is cooled to 200°F, and the thermal energy is recovered for steam generation, CO_2 separation system, and light ends fractionation. Further cooling to 100°F is effected against cooling water, and the crude mixture is then compressed to 100 psia in a single-casing centrifugal compressor. It is then preheated against oligomer product and fed to the oligomerization reactor system which consists of three packed beds in parallel with

two online and one undergoing regeneration at any given time. The reactors are operated adiabatically with an inlet temperature of 600°F.

The crude oligomer product is cooled to 100°F partly by heat interchange with feed and finally against cooling water. Most of the C_4+ components and the water present are condensed. The uncondensed vapor is recycled to the Redox reactor via a CO_2 removal system, after taking a purge for use as fuel in the steam generation system. The liquid product is fractionated to separate light ends (also used as fuel in the steam generation system) and to reduce the C_4 content of the raw gasoline/condensate to about 3 wt% (i.e., similar to the MTG product, which has a Reid vapor pressure of about 9).

Cofeed Case

The Cofeed case differs from the Redox case in the design of the oxidative coupling stage as illustrated in Figure 6.2. Two multibed reactors with intercoolers are used (one on line and the other undergoing regeneration at any given time). An air separation unit provides oxygen of 99.5% purity which is fed to the reactors in a staged manner. The mixed makeup feed and the recycle stream enter at the top of the reactor. The temperature rise in each catalyst bed is controlled by the circulating aerated water in the intercoolers and the O_2:feed ratio to each stage. The crude reactor product is cooled against the incoming reactor feed. Unlike the Redox system, no thermal energy is lost in regeneration offgas. The process sequence following the oxidative coupling stage is identical to the Redox case.

Process Discussion

Redox Case

Although we have shown a single FCC type reactor in our flow diagram (see Figure 6.1), it may be more practical and economic to have two units in parallel. Data provided by Air Products (Houdry Division) indicate that the regenerator diameter would be about 50 ft for a single unit, thereby necessitating on-site construction (compared with two shop-built units, each of 35 ft diameter). However, our cost estimates for a single Redox reactor are conservative, and therefore the effect on process economics of having two smaller units would be small.

We have assumed that the catalyst losses from the Redox reactor would be similar to an FCC unit, which is approximately 0-15-0.20 lb/b feed. The operating temperatures for the Redox reactor are significantly higher than for FCC (-1500°F instead of -1200°F), and the major challenge in development work would be to formulate a catalyst that does not agglomerate and stays fluidized at the higher temperatures.

Cofeed Case

Oxygen purity is a key factor that determines the energy costs (compressor bhp) and the capital investment for an air separation unit. We have set the O_2 purity at 99.5 vol% which requires 590 bhp/short ton of O_2 compared with, for instance, 442 bhp/short ton of O_2 at 98 vol% purity. We have done so because sufficient thermal energy is available in by-product streams and through heat recovery from the oxidative coupling reactor. A higher O_2 purity

would prohibit N_2 and inerts from air from building up in the recycle stream to the same extent with a less pure O_2 stream; thus a large purge would not be necessary.

For the Cofeed reactor we have opted for a multibed concept with intercoolers and staged oxygen feed. We judge that this system would not only lend itself best to temperature control but would also be the most economic. Among the alternatives, a cold shot system would require excessive recycle levels (thereby using greater compression energy and higher reactor volumes) and dilution with an inert component such as steam would be wasteful both in reactor space and in energy (with the steam latent heat not recoverable at high enough temperatures to be useful).

Under normal operating conditions the Cofeed reactor compositions would be well within the safe fuel-rich regime, owing to the low conversion per pass. However, an elaborate trip system would be necessary to ensure that inadvertant deviations from the safe regime do not occur. Such systems are typically used in hydrocarbon-oxygen based processes such as ethylene oxide production. We have allowed for the additional cost for this in our capital estimates.

General

As we did in our evaluation of gasoline by the MTG process (Section 3), we have kept the C_4s at a level that would give a Reid vapor pressure of about 9. Surplus C_4s are removed overhead in the light ends fractionator and used as fuel for the generation of HP steam. We judge that the total volume of C_4s disposed of in this manner is too small to justify either selling them as LPG product or converting them to alkylate.

Energy Aspects

The main energy aspects of our evaluation of the ARCO technology are shown in Table 6.4. The overall energy efficiency (HHV) basis for the Redox and Cofeed cases is quite similar--at 45.6% and 45.5%, respectively. That efficiency compares with 50.2% for our evaluation of gasoline from Mobil's MTG process and reflects the somewhat lower hydrocarbon yield (as indicated by our assumed stream flow data in Table 6.2).

The Cofeed case has slightly lower efficiency because of its higher natural gas fuel use for start-up, which follows from the larger HP steam output for turbine drives. As shown in Table 6.4, the air separation compressor accounts for this difference.

Although the Cofeed case requires a higher HP steam output, it also has a higher thermal energy recovery from the reaction because virtually no thermal energy is rejected in a regeneration offgas stream. Both processes are thus in energy balance, and any surplus HP steam (after turbine requirements are met) is used to generate electricity. We have set the thermal heat recovery for the two cases slightly below the full potential (thereby saving on capital investment costs) so that electrical energy availability in each case is close to 15 MWh/h--an amount we judge to be adequate for miscellaneous process and offsite needs.

Cost Estimates

Table 6.5 shows the breakdown of capital investment costs for both the Redox and Cofeed cases. The data are for a PEP Cost Index of 445 (mid-1986) and a U.S. Gulf Coast location. The battery limits for the two cases are very close at $286 and $291 million respectively. As shown in Table 6.5, the additional costs for an air separation plant in the Cofeed case are compensated for by a less expensive oxidative coupling section, which leads to a total cost similar to that for the Redox system. The investment costs for oligomerization and CO_2 separation are common to both cases. The total fixed capital for the two cases are $437 and $445 milliion, respectively--their proximity follows from their similar battery limits capital.

Tables 6.6 and 6.7 give the production costs in 1986 dollars for a U.S. Gulf Coast location. As discussed in Section 3, we have taken CRC to be 20%/y of TFC. At a zero natural gas cost, the cash costs for the conversion are $10.72/b (Redox case) and $10.70/b (Cofeed case). The corresponding total costs, including CRC, are $43.74/b and $44.33/b respectively. The following equations represent the cost data:

$$F_{RDX} = 11.36N + 2.57f_M + 2.14f_L + 6.01f_A + 33.02f_C \quad (6.1)$$

$$F_{COF} = 11.37N = 2.43f_M + 2.17f_L + 6.10f_A + 33.63f_C \quad (6.2)$$

where, F_{RDX} and F_{COF} are full costs in 1986 $/b, including 20%/y of TFC for CRC for the Redox and Cofeed cases. f_M, f_L, f_A, and f_C are location factors for raw materials, labor, additional cash costs and capital, respectively. All are equal to 1 for a U.S. Gulf Coast location. N is value of natural gas ($/$10^6$ Btu).

If an overall cost location factor f_O applies to all cost elements, equations 6.1 and 6.2 simplify to:

$$F_{RDX} = 11.36N + 43.74f_O \quad (6.3)$$

$$F_{COF} = 11.37N + 44.33f_O \quad (6.4)$$

Figure 6.3 illustrates the dependence of the product costs for the Redox case on natural gas values for various levels of the overall cost location factor.

Table 6.1

PRODUCT YIELDS FROM METHANE OXIDATIVE COUPLING
(Weight Percent)

	Total Product	Hydrocarbons Basis
Hydrogen	0.7	—
Ethylene	13.5	55.3
Ethane	1.9	7.8
Propane/propylene	2.3	9.4
C_4+ hydrocarbons	6.7	27.5
Water	48.6	—
Carbon dioxide	22.5	—
Carbon monoxide	3.0	—
Coke	0.8	—
	100.0	100.0

Source: ARCO Chemical Company.

Table 6.2

CONVERSION OF OLEFINS OVER ZSM-5 CATALYST
Basis: 1 atm, WHSV = 0.5–0.9, 520°–530°F
(Weight Percent)

Olefin Charge	$C_2^=$		$C_3^=$	$C_5^=$	1-$C_6^=$	1-$C_{10}^=$
$C_2^=$ Product	47.5	0*	<0.1	<0.1	<0.1	<0.1
$C_3^=$ Product	5.6	11	8	10	9	4
$C_4^=$ Product	10.6	20	28	20	20	13
$C_5^=$ Product	11.3	21	30	27	23	26
$C_6^=$ Product	6.9	13	13	15	16	20
$C_7^=$ Product	6.2	12	11	11	10	17
$C_8^=$ Product	4.1	8	6	7	8	8
$C_9^=$ Product	4.3	8	3	5	6	7
$C_{10}^=$ Unidentified	3.5	7	1	5	8	5
	100	100	100	100	100	100

* Based on converted $C_2^=$.

Source: Reference 4.

Table 6.3

GASOLINE FROM NATURAL GAS USING ARCO'S METHANE OXIDATIVE COUPLING AND OLEFINS OLIGOMERIZATION CONCEPTS: STREAM FLOWS

Plant Capacity: **8,060 b/sd of gasoline or 2.65 million b/y (equivalent to ~311,000 mt/y) at a 0.90 stream factor**

		Stream Flows (lb/h)								
	Molecular Weight	(1) Natural Gas Feed	(2) Redox Recycle	(3) Reactor Feed	(4) Air Feed	(5) Regenerated Off Gas	(6) Redox Product	(7) Condensate 1	(8) Compression Feed	(9) Condensate 2
Water	18.02						219,779	201,572	18,207	7,748
Nitrogen + inerts	28.01	2,061	176,506	178,567	1,124,614	1,124,614	178,567		178,567	
Oxygen	32.00				341,486	82,554				
Hydrogen	2.02		2,862	2,862			3,926		3,926	
Methane	16.04	143,010	493,957	636,967			499,851		499,851	
Carbon monoxide	28.01		14,147	14,147			14,312		14,312	
Carbon dioxide	44.01	2,261	871	3,132		13,127	105,058		105,058	
Ethylene	28.05		803	803			82,900		82,900	
Ethane	30.07	7,619	11,008	18,627			8,820		8,820	
Propylene	42.08		826	826			9,645		9,645	
Propane	44.10	6,183	1,944	8,127			794		794	
1,3-Butadiene	54.09						3,560		3,560	
Butene	56.11		1,502	1,502			1,378		1,378	
Butane	58.12		2,811	2,811			508		508	
Pentane	72.15		159	159			34		34	
Benzenes	78.11						25,016		25,016	
Gasoline			14	14						
Total		161,135	707,210	868,345	1,466,100	1,200,295	1,134,149	201,572	932,577	7,748

		Stream Flows (lb/h)								
	Molecular Weight	(10) Oligomerization Feed	(11) Oligomerization Liquid Product	(12) Oligomerization Product Vapor	(13) Fuel Purge	(14) CO_2 Removal Feed	(15) CO_2 Gas	(16) Fractionation Feed	(17) Light Ends	(18) Gasoline Product
Water	18.02	10,459	10,459							
Nitrogen + inerts	28.01	178,567		178,567	2,061	176,506				
Oxygen	32.00									
Hydrogen	2.02	3,926		2,895	33	2,862				
Methane	16.04	499,851		499,723	5,766	493,957				
Carbon monoxide	28.01	14,312		14,312	165	14,147				
Carbon dioxide	44.01	105,058		105,058	1,212	103,846	102,975			
Ethylene	28.05	82,900		810	7	803				
Ethane	30.07	8,820	1	11,137	129	11,008		1	1	
Propylene	42.08	9,645	8	836	10	826		8	8	
Propane	44.10	794	12	1,967	23	1,944		12	12	
1,3-Butadiene	54.09	3,560								
Butene	56.11	1,378	5,699	1,520	18	1,502		5,699	4,422	1,277
Butane	58.12	508	4,195	2,844	33	2,811		4,195	2,665	1,330
Pentane	72.15	34	16,975	161	2	159		16,975	509	16,466
Benzenes	78.11	25,016	25,015					25,015		67,838
Gasoline			42,822	14		14		42,822		
Total		924,829	105,186	819,843	9,468	810,185	102,975	94,727	7,617	86,910

Table 6.4

GASOLINE FROM NATURAL GAS USING ARCO'S METHANE OXIDATIVE COUPLING AND OLEFINS OLIGOMERIZATION CONCEPTS: MAIN ENERGY FEATURES OF SRI EVALUATION

Process Aspect	Main Quantitative Data	Redox Case 10^6 Btu/h	Cofeed Case 10^6 Btu/h
Overall energy efficiency	Natural gas feed	3,792	3,792
	Natural gas fuel*	21	26
	Total (HHV basis)	3,813	3,818
	Raw gasoline (HHV)	1,738	1,738
	Energy efficiency (HHV basis)	45.6%	45.5%
Energy for HP steam† system	Total required	970	1,230
	Source		
	Heat recovery from redox	730	
	Heat recovery from cofeed reaction		990
	From by-product combustion	240	240
	Total (net)	970	1,230
Exotherm in redox reactor (used in heating feed, recycle, and air)		1,388	As in the Redox, case, but used in steam generation, CO_2 separation, and light ends separation.
Exotherm in oligomerization (used in heating feed)		112	As in the Redox case

Use of HP steam:

Redox Case				Cofeed Case			
User	lb/h	bhp	MWh/h	User	lb/h	bhp	MWh/h
Air compressor	339,900	55,000	—	Air separation compressor	508,610	82,300	—
Olig. feed compressor	160,680	26,000	—	Olig. feed compressor	160,680	26,000	—
Power generation‡	125,220	20,300	14.8	Power generation	125,220	20,300	14.8
Total	625,800	101,300			794,510	128,600	

Other principal thermal needs (met from Redox heat recovery)

	10^6 Btu	10^6 Btu
CO_2 separation system	97	As in the Redox case
Light ends separation	15	As in the Redox case

* Natural gas is used for steam generation only during start-up.

† At 1000°F, 1100 psia.

‡ For all battery limits and offsites needs.

Table 8.5

GASOLINE FROM NATURAL GAS USING ARCO'S METHANE OXIDATIVE COUPLING AND OLEFINS OLIGOMERIZATION CONCEPTS: CAPITAL INVESTMENT

Plant Capacity: 8,060 b/sd of gasoline or 2.64 million b/y (equivalent to ~311,000 mt/y) at a 0.9 stream factor
PEP Cost Index = 445; U.S. Gulf Coast Location

	Millions of Dollars	
	Redox	Cofeed
Battery limits		
Air separation	---	95
Oxidative coupling section (includes steam generation and recycle compressor)	173	83
Oligomerization	94	94
CO_2 separation	19	19
Total battery limits	286	291
Offsites		
Waste treatment and utilities	46	47
General service facilities	78	80
Tankage	27	27
Total offsites	151	154
Total fixed capital	437	445

Table 6.6

GASOLINE FROM NATURAL GAS USING ARCO'S METHANE OXIDATIVE COUPLING AND OLEFINS OLIGOMERIZATION CONCEPTS

REDOX CASE: PRODUCTION COSTS

Plant Capacity: **8,060 b/sd of gasoline or 2.65 million b/y (equivalent to ~311,000 mt/y) at a 0.9 stream factor**
PEP Cost Index = 445; U.S. Gulf Coast Location

	Millions of Dollars	
Capital investment		
Battery limits (BL)	286	
Offsites	151	
Total fixed capital (TFC)	437	
	Cents per Pound	**Dollars per Barrel**
Production Costs		
Raw materials and utilities		
Natural gas, $N/10^6 Btu	4.387N	11.36N
Redox catalyst, $1/lb	0.08	0.200
Oligomerization catalyst, $10/lb	0.06	0.155
Monoethanolamine, $0.5/lb	0.02	0.061
Maintenance materials, 1.5%/y of BL cost	0.63	1.621
Operating materials, miscellaneous	0.20	0.518
Utilities	nil	nil
Variable cost	4.387N+0.99	11.36N+2.566
Labor		
Operating labor, 6 men/shift, $21.82/man-hour	0.17	0.432
Maintenance labor, 1.5%/y of BL cost	0.63	1.621
Control laboratory, 20% of operating labor	0.03	0.086
Total labor	0.83	2.139
Additional cash costs		
Plant overhead, 80% of total labor	0.66	1.711
Taxes and insurance, 2%/y of TFC	1.27	3.302
G&A, sales, research	0.38	1.000
Total cash cost	4.387N+4.13	11.36N+10.718
Capital related costs (CRC), 20%/y of TFC	12.76	33.023
Total cost (including CRC)	4.387N+16.89	11.36N+43.741

Table 6.7

GASOLINE FROM NATURAL GAS USING ARCO'S METHANE OXIDATIVE COUPLING AND OLEFINS OLIGOMERIZATION CONCEPTS

COFEED CASE: PRODUCTION COSTS

Plant Capacity: **8,060 b/sd of gasoline or 2.65 million b/y (equivalent to ~311,000 mt/y) at a 0.9 stream factor**
PEP Cost Index = 445; U.S. Gulf Coast Location

	Millions of Dollars	
Capital investment		
Battery limits (BL)	291	
Offsites	154	
Total fixed capital (TFC)	445	
	Cents per Pound	**Dollars per Barrel**
Production Costs		
Raw materials and utilities		
Natural gas, $N/10⁶ Btu	4.393N	11.37N
Redox catalyst, $1/lb	0.02	0.040
Oligomerization catalyst, $10/lb	0.08	0.166
Monoethanolamine, $0.5/lb	0.02	0.061
Maintenance materials, 1.5%/y of BL cost	0.64	1.649
Operating materials, miscellaneous	0.20	0.518
Utilities	nil	nil
Variable cost	4.393N+0.94	11.37N+2.434
Labor:		
Operating labor, 6 men/shift, $21.82/man-hour	0.17	0.432
Maintenance labor, 1.5%/y of BL cost	0.64	1.649
Control laboratory, 20% of operating labor	0.03	0.086
Total labor	0.84	2.167
Additional cash costs		
Plant overhead, 80% of total labor	0.67	1.734
Taxes and insurance, 2%/y of TFC	1.30	3.363
G&A, sales, research	0.38	1.000
Total cash cost	4.393N+4.13	11.37N+10.698
Capital related costs (CRC), 20%/y of TFC	12.99	33.628
Total cost (including CRC)	4.393N+17.12	11.37N+44.326

Figure 6.1
GASOLINE FROM NATURAL GAS USING ARCO'S CONCEPT OF OXIDATIVE COUPLING/OLEFIN OLIGOMERIZATION
(Redox Case)

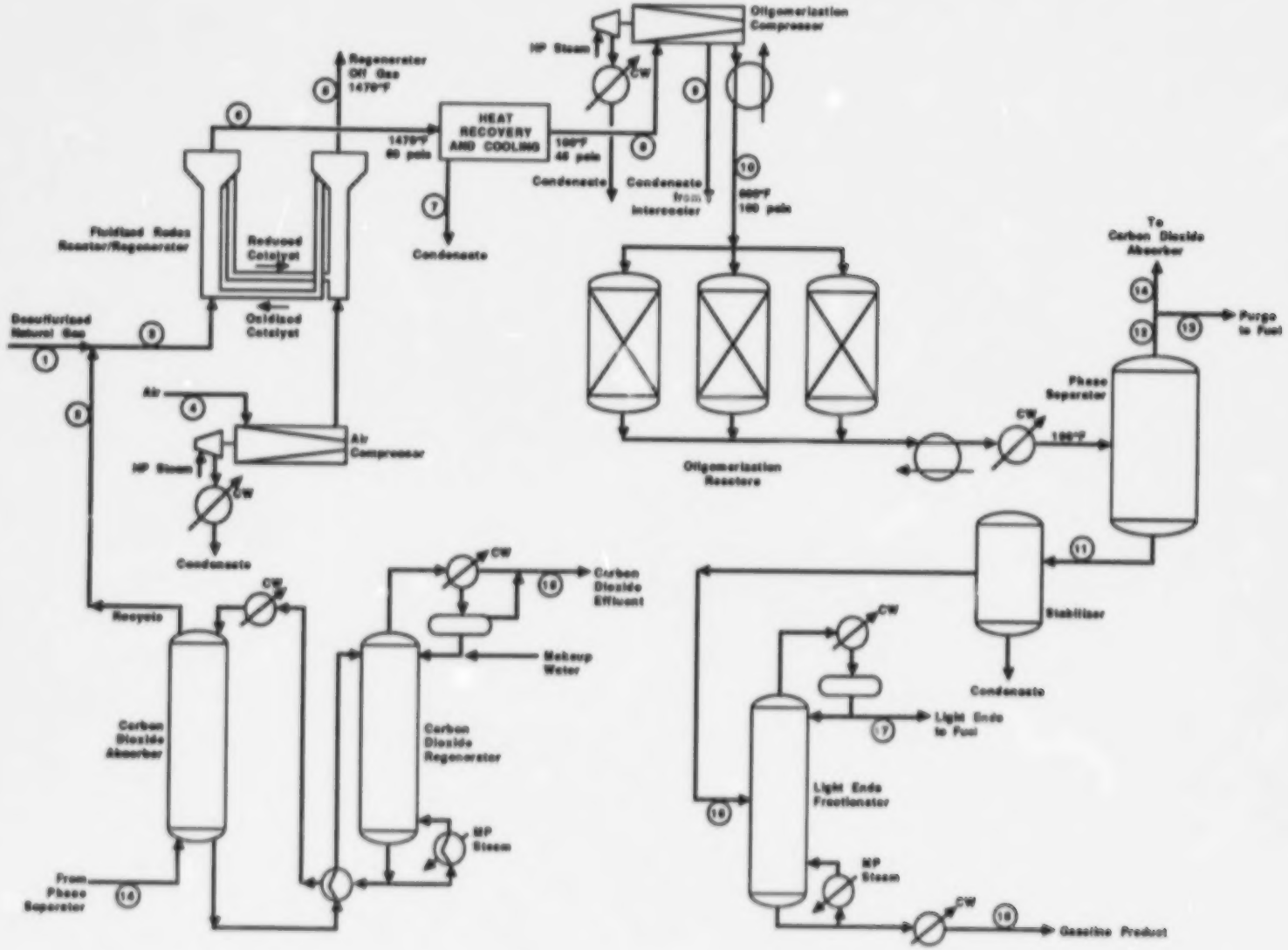


Figure 6.2
GASOLINE FROM NATURAL GAS USING ARCO'S CONCEPT OF OXIDATIVE COUPLING/OLEFIN OLIGOMERIZATION
(Cofeed Case)

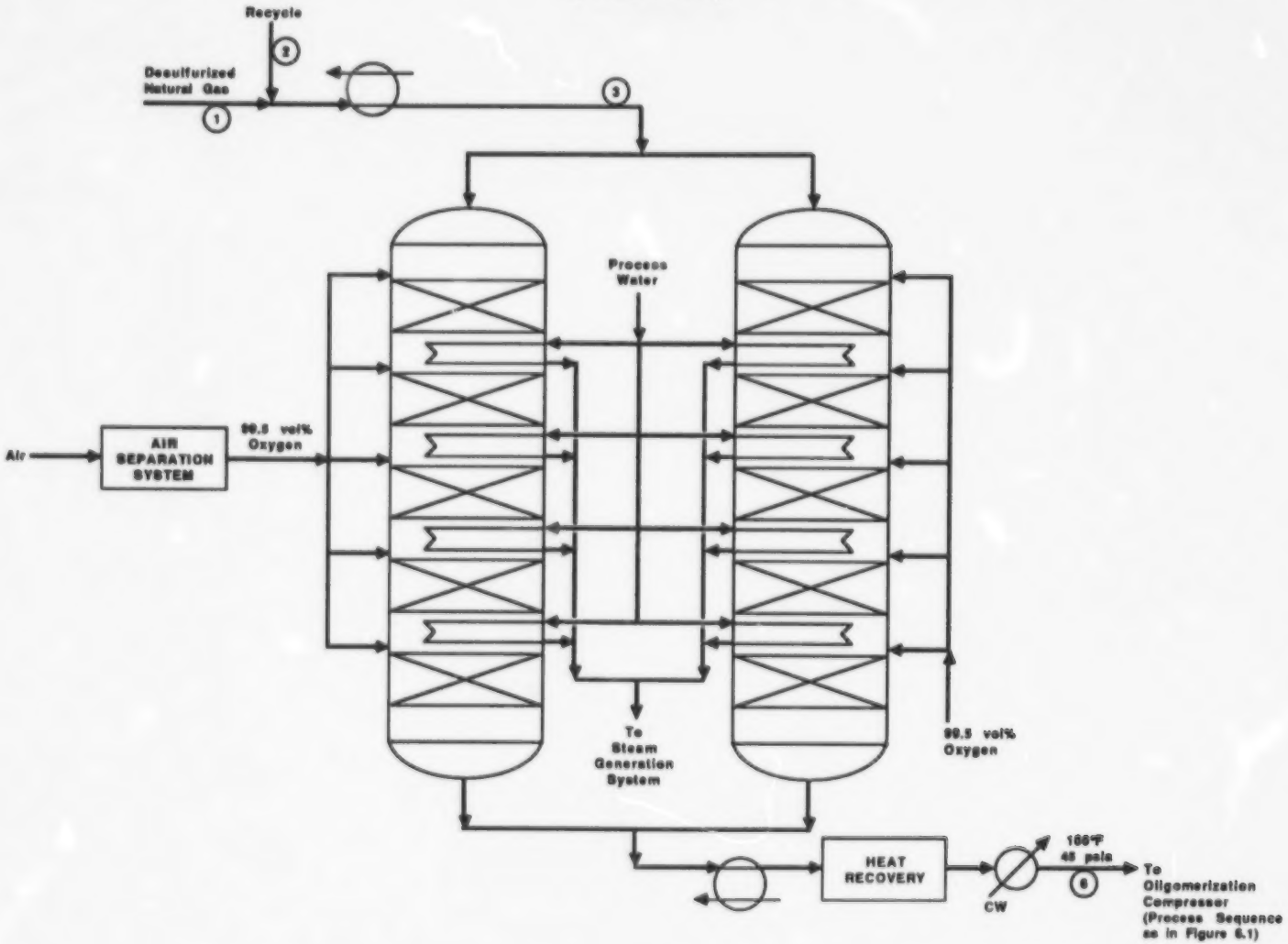
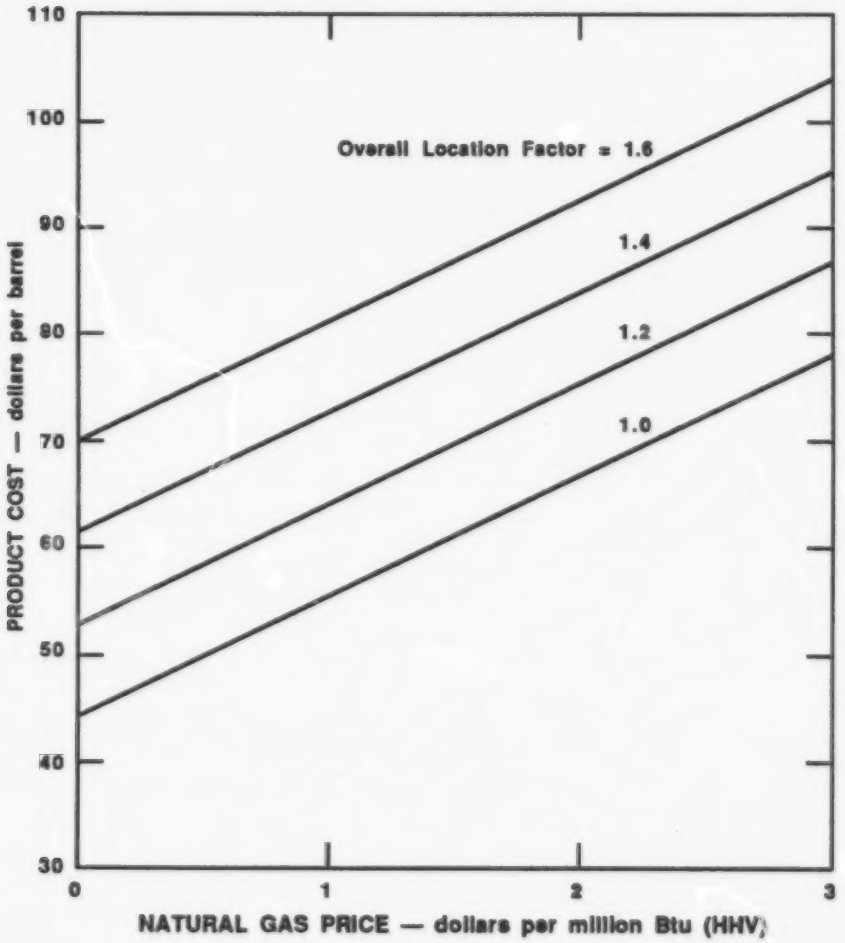


Figure 6.3

GASOLINE FROM NATURAL GAS USING ARCO'S CONCEPT OF METHANE OXIDATIVE COUPLING/OLEFIN OLIGOMERIZATION:
Product Cost as a Function of Natural Gas Price and Location Factor



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7 MIXED ALCOHOLS FROM NATURAL GAS USING THE DOW/UNION CARBIDE PROCESS

The production of oxygenated octane improvers is of interest because of the phasing out of lead from the gasoline. The United States has been in the forefront of the trend, but Western Europe and Japan are also moving toward lead-free gasoline. A product mixture of C_2 to C_5 alcohols and methanol helps overcome phase separation with water and improves the Reid vapor pressure deficit. Such a mixture, which can be made from syngas, could thus represent an attractive investment option in using remote natural gas.

Several companies have been active in developing processes for mixed alcohols from syngas, notably Dow Chemical and Union Carbide Corporation (UCC) in the United States, Institute Francais du Petrole (IFP) in France, and Snamprogetti in Italy. Others in the field include Lurgi (West Germany), which has modified its methanol synthesis catalyst to permit coproduction of higher alcohols; and Texaco (United States), which has patented a ruthenium-based catalyst for the synthesis (see Table 7.1 for a description of the various companies' technology positions). Dow's recent announcements of a process [1-3] that uses modified Fischer-Tropsch (FT) catalysts (based on molybdenum) appear to be of particular interest in terms of the indicated space-time yields, selectivities to the desired products, low water content in the reaction product, and flexibility in methanol/higher alcohols ratios. Although the original disclosures were made by Dow alone, the process has now become a Dow-UCC joint venture and is referred to as the "Dow/UCC mixed alcohols process" [4].* The partnership brings together the catalyst know-how and patent positions of the two companies in this area.

In this section we evaluate the Dow/UCC mixed alcohols process on the basis of using natural gas steam reforming for syngas generation. The assumed methanol/higher alcohols ratio is 30:70 by weight. Nonproprietary data for the Dow/UCC process were made available to us for this evaluation [4]. Although Dow and UCC have used partial oxidation for syngas generation in their evaluation, they agree with SRI that other approaches merit examination. In addition to steam reforming, they include combined primary reforming with steam and secondary reforming with oxygen.

Chemistry

C_1-C_5 alcohols can be synthesized from syngas in the presence of supported rhodium catalysts, modified methanol catalysts, and modified FT catalysts. The Dow catalysts are molybdenum based and belong to the modified Fischer-Tropsch category. The synthesis of alcohols follows a chain-growth mechanism in which linked methylene (CH_2) groups of varying lengths are formed. Unlike those in traditional FT synthesis, the chains are terminated (for the most part) by hydroxyl (OH) or primary alcohol groups, not by alpha olefin groups. Thus,

* Dow/UCC have also used the name SYGMAL (syngas-mixed alcohols) for the process.

primary alcohols instead of paraffins are the dominant products. The general stoichiometry for alcohols formation can be represented as follows:

$$nCO + 2nH_2 \rightarrow C_n H_{2n+1} OH + (n-1)H_2O. \quad (7.1)$$

The general stoichiometry for paraffins formation is:

$$nCO + (2n+1)H_2 \rightarrow C_n H_{2n+2} + nH_2O. \quad (7.2)$$

Both reactions 7.1 and 7.2 are highly exothermic.

In addition to the principal reactions, which lead to the formation of alcohols and paraffins, the CO reacts with the water formed to produce CO_2 and H_2 according to the equilibrium of the shift reaction:

$$CO + H_2O \leftrightarrows CO_2 + H_2. \quad (7.3)$$

Review of the Processes

As stated earlier, Dow/UCC, IFP, and Snamprogetti are undertaking advanced process development for the commercializaton of their respective concepts. Snamprogetti has operated a 40 mt/d pilot plant that produces mixed alcohols containing 20–50% C_2+ higher alcohols [3]. Although it is still in the laboratory stage of development, IFP states its technology is sufficiently advanced for commercialization, and IFP's publication of a definitive picture of the process and associated economics [5–7], followed by some pilot scale work in collaboration with Idemitsu, Japan [8], supports that claim. Although Dow first announced its process in November 1984 [1], it has since completed development work relating to catalysts. Dow used two high-pressure pilot scale reactors--a fluidized-bed reactor and a fixed bed reactor [4].

In addition to these three companies, several others have patents or publications in this area. Table 7.1 lists companies with well-defined technical positions in the synthesis of mixed alcohols from syngas.

In a broad sense, two research paths have been followed. Rhodium-based catalysts, as developed by UCC, Sagami, and Hoechst, tend to be more selective for ethanol synthesis, but also lead to other C_2 oxygenates (acetaldehyde and acetic acid) and enhanced levels of methane in the reaction product. The current selectivities and catalyst productivities do not appear to be high enough for the economic production of octane improvers. Nor do they provide a basis for a competitive alternative to conventional ethanol synthesis by ethylene hydration.

Modified methanol catalysts (Lurgi, IFP, and Snamprogetti) or modified FT catalysts (Dow) are more effective in producing C_1–C_5 alcohol mixtures. Dow's modified FT catalyst system, which is based on molybdenum sulfide, offers greater flexibility in terms of methanol:higher alcohols ratios and higher selectivities to the desired liquid alcohols product. The catalyst system also exhibits homologation activity. The three principal users of modified methanol catalysts (IFP, Lurgi, and Snamprogetti) make similar claims for product yields. However, Snamprogetti's process uses substantially higher pressures and also exhibits a lower catalyst productivity than does IFP's. (We found no catalyst productivity data for Lurgi's process in the published literature.) Although the Dow/UCC process has a lower catalyst productivity than

does the IFP process (20–35 lb of alcohols/ft³–h, depending on reaction conditions, compared with 60 lb/ft³–h), that disadvantage is offset by the other positive features stated earlier.

Texaco's ruthenium–based catalyst systems contrast sharply with the nonprecious metal catalysts (based on Cu and Mo) in the high pressures they require (6615 psia, compared with 1500–2000 psia for Dow/UCC and 850–1450 for IFP) and the generally higher levels of nonalcohol oxygenates, mainly methyl acetate and ethyl acetate (12–39 wt%), they produce. Although the catalyst productivity is good (62 lb/ft³–h), the Texaco catalyst system is a liquid phase and does not function heterogeneously as the others do. Catalyst recovery and regeneration would also be needed, which could be an economic disadvantage.

Use of Modular Approach for Evaluation

SRI's overall process concept is illustrated by the block diagram in Figure 7.1. The blocks represent process modules that are roughly equivalent to the individual process sections used in our standard cost–evaluation procedure. For this review, we have adopted a modular approach (instead of using a detailed flow sheet) for estimating capital investment costs. For this purpose, we have used data available to SRI on each of these modules. The details are discussed later under "Cost Estimates." We prepared material and energy balances to define the parameters for the modules and to provide data on feedstock and utilities use.

Description of the SRI Process Concept

The essential design features of the process modules (as illustrated by Figure 7.1) and the underlying assumptions are enumerated in Table 7.2.

The stream flows are presented in Table 7.3, for a base case mixed alcohols output of ~1.5 billion (10^9) lb/y at a 0.9 stream factor, equivalent to about 16,600 b/sd. Expressed on a methanol equivalent basis, the natural gas feedstock rate to the reformer is that for 2,500 mt/d of methanol, which is our basis for the largest single train plant as discussed in Section 5.

Module 1 generates syngas by steam reforming at conditions close to those used for ammonia manufacture (400 psia, 1560°F) and at pressures somewhat higher than the 250–300 psi used for methanol. The resulting higher methane slippage (i.e., unconverted methane in the dry reformer product) is compensated for by savings on compression. A high CO_2:natural gas ratio (3.3:1) is used to give the desired low H_2:CO ratio (1.36:1) in the syngas product. Most of CO_2 is recycle material, but a small amount (slightly less than 4% of the total CO_2 in the reformer feed) is extracted from reformer flue gases (Module 7). A balanced configuration with no CO_2 import is possible, but would entail a larger fuel purge and hence higher makeup syngas rates. We have set the purge level at about 16% of the makeup syngas rate, which leads to a methane content in the synthesis feed similar to that in the Dow evaluation [4].

The cooled, virtually dry gas from syngas generation (Module 1), which contains nearly 40% CO_2, is processed for CO_2 removal in Module 2. As indicated in Table 7.2, we have assumed that a Selexol® system is used to reduce the CO_2 level in the unabsorbed gas to 100 ppm. (Our choice of a physical solvent process such as Selexol® is based on energy considerations. Chemical solvent processes using amines or K_2CO_3 can also be economical when surplus low–temperature energy is available.) The CO_2 is recycled to the steam reformer, and the fresh syngas is compressed and fed to alcohols synthesis (Module 3) along with recycle

syngas and a recycle CO-rich stream. The H_2:CO ratio of the total synthesis feed is 1.1255:1. The CO conversion, based on total feed, is 40%. The formation of CO_2 and H_2 (by reaction 7.3) causes the H_2:CO consumption ratio to be low, at the same time leading to reduced water content in the alcohols product. The overall reaction is highly exothermic (ΔH = 24.3 kcal/mol of CO converted). This energy is recovered for steam generation.

The crude synthesis product is cooled against the synthesis feed, with a 30 Fahrenheit degrees approach, and is purified in Module 4. Phase separation is effected by chilling to −40°F, which ensures less than 1,000 ppm of alcohols in the uncondensed gas. The condensed liquid phase contains an appreciable amount of dissolved CO_2 (estimated at 30 mol% of the mixed alcohols), which is flashed during the depressurization to 15 psia. The flashed CO_2 is recycled to the reformer. The CO_2-free, wet alcohols product, which contains 3.7 wt% water, is dried on molecular sieves, such as UCC's type 3A, to 0.1 wt% water.

The uncondensed gas from Module 4 (stream 13) goes to Module 5 (CO_2 Separation-II) for the separation of CO_2. As we did for the reformer product, we have assumed that a Selexol® system is used. We consider it necessary to have two CO_2-removal modules because of the significantly different pressures of the two streams. Unlike reformer stream 7, uncondensed gas stream 13 has a much lower CO_2 content (slightly below 5%), but that is compensated for by its higher pressure, which gives a sufficiently high CO_2 partial pressure (94 psia, compared with 150 psia for stream 7) for Selexol® to be applicable. A major part of the CO_2-free gas from Module 5 is recycled to alcohols synthesis (Module 3) and the balance (13.6% of total stream) is subjected to CO recovery in Module 6. The recovered CO is recycled to the synthesis reactor.

A syngas purge from Module 5 (stream 16) is necessary to prevent the buildup of methane, ethane, and nitrogen in the alcohols synthesis reactor. Its direct purge would lead to a loss of valuable syngas; therefore, we have concluded that the recovery and recycle of CO from this stream are economically justified because higher carbon efficiencies would result. Moreover, the recycle of CO allows the reformer to be operated more economically at higher syngas H_2:CO ratios, with a reduction in the need for imported CO_2. We therefore included Module 6 in our design concept for the separation of CO before the purge is drawn. A cryogenic system based on a liquid methane wash is assumed. It separates most of the H_2 and CH_4 in stream 17 for purge and recovers 99% of the CO for recycle to alcohols synthesis.

From the stream flows given in Table 7.3, the overall carbon conversion efficiency to useful product (expressed as C atoms in alcohols product/C atoms in natural gas feed and imported CO_2) is 80.6%. That efficiency, in turn, relates to a synthesis reactor carbon efficiency of 85% on a CO_2-free basis. The carbon loss in the purge is thus 19.4%. Current methanol technology based on natural gas achieves an overall carbon efficiency of 87%. Carbon efficiencies (including the carbon input from reformer furnace fuel) are discussed further below.

Energy Aspects

The main quantitative data relating to the broad energy aspects of the SRI process concept are presented in Table 7.4. We have assumed that the recovered heat energy is used for regenerating CO_2 in the three CO_2 separation modules and for meeting part of the energy requirements for steam generation and reformer preheat. The balance comes from the fuel system, of which the energy provided by the purge stream constitutes a maior part (61.7%).

Direct natural gas fuel thus amounts to about 38.3% of the total fuel system. We have also assumed that the steam generated is used to drive the turbines for electricity generation and for the CO_2 and makeup syngas compression. The steam consumption rates and turbine brake horsepower are also shown in Table 7.4. The total electricity generated is -20 MWh/h, which we estimate would be required to meet the various battery limits and offsite duties (e.g., recycle syngas compression, combustion air blower, flue gas extractor, boiler feed water pumps, cooling water pumps).

Taking into account the natural gas used as fuel, the total use of natural gas energy (HHV basis) corresponds to 20,990 Btu/lb of mixed alcohols. That figure compares with the 21,850 Btu/lb indicated by Dow for a similar product by a process that uses partial oxidation for syngas generation. It also compares with 14,850 Btu/lb for methanol by the ICI high energy efficiency process. The energy characteristics of the mixed alcohols product are shown in Table 7.5. The energy efficiency of the process which is defined as

(HHV of mixed alcohols product)/(HHV of natural gas feed + fuel),

is equivalent to 60.2%, as opposed to 69.4% for methanol by the ICI process. Compared with the HHV of premium unleaded gasoline of 130,000 Btu/gal, the HHV of the alcohols mixture is about 83,860 Btu/gal. That value is 23.9% higher than the HHV of 67,680 Btu/gal for methanol and is equivalent to 95.6% of the HHV of 88,440 Btu/gal for ethanol.

Cost Estimates

As discussed before, we have estimated the battery limits capital costs for the modules from data available to SRI. For the base case of 1.5 billion (10^9) lb/y mixed alcohols (-16,600 b/sd), the battery limiting capital is $281 million for a U.S. Gulf Coast location and a PEP Cost Index of 445 (mid-1986).

The offsites capital on the same basis is $176 million. The breakdown is shown in Table 7.6. Production costs are presented in Table 7.7. With natural gas at zero value the cash costs are $6.23/b, and the total cost (including 20%/y of TFC for capital related charges) are -$23/b.

The cost equation is as follows:

$$F_{MA} = 5.77N + 1.61f_M + 1.08f_L + 3.54f_A + 16.75f_C \quad (7.4)$$

where, F_{MA} is the full cost in 1986 $/b, including 20%/y of TFC for CRC. f_M, f_L, f_A, and f_C are location factors for raw materials, labor, additional cash costs and capital, respectively (all are equal to 1 for a U.S. Gulf Coast location). N is the value of natural gas ($/$10^6$ Btu).

If an overall cost location factor f_O applies to all cost elements, equation 7.4 simplifies to:

$$F_{MA} = 5.77N + 22.99f_C \quad (7.5)$$

Figure 7.2 illustrates the dependence of mixed alcohol product costs on natural gas values for various levels of the overall cost location factor.

Table 7.1

MIXED ALCOHOLS FROM NATURAL GAS USING THE DOW/UCC PROCESS: THE TECHNOLOGY POSITIONS OF ACTIVE COMPANIES

Company	References	Catalyst Systems	Key Technical Features
Lurgi (West Germany)	9,10	Modified methanol synthesis catalyst based on Cu.	Under conditions similar to those of methanol synthesis, but with syngas H_2/CO ratios slightly above 1, the product mixture comprises 53.5 wt% methanol and 41.9 wt% C_2–C_6 alcohols.
Union Carbide (U.S.A.)	11, 27–32	Mainly Rh or combinations with Fe, Mn, or Mo on a carrier such as silica gel, gamma-alumina, or C.	Reaction conditions are 300–350°C, 1000–2500 psia. The product is a mixture of ethanol, acetic acid, acetaldehyde, and ethyl acetate; CO selectivity to ethanol (including ethanol equivalent of ethyl acetate) is 60%; space-time yield of ethanol is 30 lb/ft³–h.
Sagami Research Center (Japan)	12, 13, 33	Rhodium carbonyl (in some patent examples with niobium) cluster on a La, Ti, or Zr oxide carrier.	Typically, reaction conditions are 200–300°C and 1–50 atm; products are mainly methanol, ethanol, and methane; high selectivities to ethanol (up to 61%) are claimed, with total selectivity to alcohols slightly above 90%; CO per pass conversions and space-time yields are low.
IFP (France)	5, 7, 14–17	Mixed oxides of Cu and Co as key components.	Typically, reaction conditions are 260–320°C and 850–1450 psia. Per pass conversions of CO are 12–18%, and selectivities to alcohols are 70–75%; the proportion of C_2–C_4 alcohols is 30–50 wt% in mixture; maximum indicated catalyst productivity of alcohols is about 60 lb/ft³–h.
Hoechst (West Germany)	18–20	Rh on a silicate support (e.g., $MgSiO_3$) with various promoters such as Zr, Hf, La, Pt, Cr, and Hg.	At 275°C and 100 bars, the CO selectivity to ethanol is as high as 74.5%, and the space-time yield for mixed oxygenates is about 31 lb/ft³–h.
Snamprogetti (Italy)	21, 22	Mixed Zn–Cr–X oxides for first stage synthesis and mixed Zn–Cr–Cu oxides for the second stage.	A two-stage synthesis with different catalyst systems is used; at 410°C and 260 atm in the first stage and 260°C in the second stage, the total CO conversion is 17%, and selectivity to mixed alcohols is 71%; the proportion of C_2–C_4 alcohols in the mixture is 20–40%; alcohols space-time yield is 12 lb/ft³–h.
Texaco (A.)	23–25	Liquid phase system, based on ruthenium oxide in tetrabutyl phosphonium halide and containing halogen-free compounds of Ti, Zr, Mn, and Re or a cobalt derivative.	At 220–240°C and 450 atm, syngas conversions are 40%, with a carbon selectivity to oxygenated products (mainly C_1–C_3 alcohols) typically 75% and productivity of liquids 62 lb/ft³–h.
Dow (A.)	1–4, 26	Modified FT catalysts based on MoS_2, promoted with an alkali or alkaline earth element (preferably K as its oxide).	Depending on the methanol/higher alcohols ratio desired, operating conditions are 570–590°C and 1500–2000 psia. H_2:CO feed ratios are 1.1:1.2; CO per pass conversions are 20–40%, with selectivities to mixed alcohols of 85% (CO_2 free basis); the methanol content of the mixture can be varied in 30–70 wt% range; catalyst productivity is 20–35 lb/ft³–h, depending on reaction conditions.

Table 7.2

MIXED ALCOHOLS FROM NATURAL GAS USING THE DOW/UCC PROCESS: SRI PROCESS CONCEPT--DESIGN FEATURES AND ASSUMPTIONS

Process Module	Design Features and Assumptions
1. Syngas generation	Nickel catalyzed steam reforming of a mixture of natural gas and CO_2 (mainly recycle) takes place in a conventional gas fired furnace reactor. Heat recovery in the cooling of reformer product and flue gases provides reaction preheat and generates steam for process and compressor turbines. Reformer operating conditions assumed are: Temperatures Inlet 1000°F Exit 1560°F Pressures Inlet 430 psia Exit 400 psia Steam:carbon ratio (with respect to natural gas feed) = 4 (molar) Feed natural gas:CO_2 ratio = 1:3.3 (molar) under the above conditions; for a 20°F approach to equilibrium the methane slippage is just below 1% in dry reformer product and the H_2:CO ratio = 1.36:1.
2. CO_2 separation-I	The Selexol® process uses a proprietary physical absorbent (DME of polyethylene glycol). Assumptions are: Absorption at 100°F and 390 psia Regeneration at 100°F and 15 psia Residual CO_2 level in treated gas--100 ppm
3. Alcohols synthesis	The multitubular packed reactor is cooled by circulating water and contains MoS_2 based catalyst. Feed to the reactor comprises dry makeup syngas from Module 1, recycle synthesis gas, and a recycle CO-rich stream. Assumed operating conditions for the reactor are: Temperature Inlet 560°F Exit 590°F Pressure 2000 psia Feed H_2:CO ratio = 1.1255:1 Synthesis reactor performance in terms of CO conversion and product selectivities follows: CO conversion 40%

Table 7.2 (Concluded)

Process Module	Design Features and Assumptions
3. Alcohols synthesis (Continued)	Product selectivities based on CO converted

	Mol%
Carbon dioxide	32.00
Methane	9.45
Ethane	0.75
Methanol	13.46
Ethanol	28.08
Propanols	9.32
Butanols	3.13
C_5 alcohols	1.63
Methyl acetate	1.16
Ethyl acetate	1.02
Total	100.00

These selectivities correspond to 85% liquid products (alcohols + esters) and 15% gas products (CH_4 and C_2H_6) on a CO_2–free basis. The liquid product contains slightly more than 30 wt% methanol on a dry basis. The water level in the wet alcohols/esters product is calculated to be 3.7%. (Actual water levels can be lower, which gives a closer approach to the equilibrium of the CO shift reaction.)

4. Product purification — The system is based on phase separation of synthesis product by cooling to –40°F. The cooled liquid product is depressurized to flash off dissolved gases (principally CO_2). The wet alcohols product is dried on molecular sieves to a water content of 0.1 wt%.

5. CO_2 separation–II — This system removes the CO_2 from the gas leaving Module 4. A Selexol® system is used as before, but with an absorber gas inlet pressure of 1970 psia. The CO_2 level in absorber exit gas is 100 ppm.

6. CO recovery — The purge from CO_2–free synthesis product is processed in this module for CO recovery. The module comprises a cryogenic methane wash system, which recovers 99% of the CO present in the feed in a stream of 93.2% purity with N_2 as the principal impurity (6.4%). The residual fuel stream, essentially hydrogen and methane, corresponds to 15.6% of makeup syngas.

7. CO_2 separation–III — This system recovers CO_2 from reformer flue gas. A monoethanolamine based system is used, and the quantity of CO_2 recovered is set by the desired H_2:CO ratio of 1.36:1.

Table 7.3

MIXED ALCOHOLS FROM NATURAL GAS USING THE DOW/UCC PROCESS: STREAM FLOWS

Plant Capacity: 16,600 b/sd or 5.45 million b/y (equivalent to ~690,000 mt/y) at a 0.90 stream factor

		Stream Flows (lb-mol/h)								
		(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
	Molecular Weight	Natural Gas Feed	Natural Gas Fuel	CO_2 Import	Reformer Steam	Total CO_2 Recycle	Reformer Feed	Dry Reformer Product	Recycle Synthesis Product	Makeup Syngas
Hydrogen	2.02	—	—	—	—	—	—	18,636.36	19,886.24	18,636.36
Carbon monoxide	28.01	—	—	—	—	—	—	13,722.48	2,688.92	13,722.48
Carbon dioxide	44.01	46.05	9.69	1,088.37	—	26,153.36	27,287.78	21,769.74	—	—
Methane	16.04	7,858.74	1,654.21	—	—	—	7,858.74	482.55	10,974.24	482.55
Ethane	30.07	227.94	47.99	—	—	—	227.94	—	316.58	—
Propane +	44.10	125.40	26.39	—	—	—	125.40	—	—	—
Nitrogen inerts	28.01	65.60	13.80	—	—	—	65.60	65.60	1,602.89	65.60
Oxygen	32.00	—	—	—	—	—	—	—	—	—
Water	18.02	—	—	—	36,441.05	—	36,441.08	—	—	—
Methanol	32.04	—	—	—	—	—	—	—	—	—
Ethanol	46.07	—	—	—	—	—	—	—	—	—
Propanols	60.10	—	—	—	—	—	—	—	—	—
Butanols	74.12	—	—	—	—	—	—	—	—	—
C_5 alcohols	88.15	—	—	—	—	—	—	—	—	—
Methyl acetate	74.12	—	—	—	—	—	—	—	—	—
Ethyl acetate	88.15	—	—	—	—	—	—	—	—	—
Total		8,323.73	1,752.08	1,088.37	36,441.05	26,153.36	72,006.54	54,675.73	50,448.87	32,906.99

		Stream Flows (lb-mol/h)								
		(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)
	Molecular Weight	CO_2 Recycle	Synthesis Feed	Synthesis Product	Gas Product	Liquid Product	CO_2 from Separation II	CO_2 Free Gas	CO Recovery Feed	Fuel Purge
Hydrogen	2.02	8.28	38,530.88	23,112.89	23,112.89	—	—	23,112.89	3,226.65	3,218.37
Carbon monoxide	28.01	2,843.16	34,234.56	20,535.76	20,535.76	—	—	20,535.76	2,866.85	23.69
Carbon dioxide	44.01	—	—	4,383.60	2,930.40	1,453.20	2,930.40	trace	—	—
Methane	16.04	3.32	11,460.11	12,755.22	12,755.22	—	—	12,755.22	1,780.98	1,777.67
Ethane	30.07	—	316.58	366.27	366.27	—	—	366.27	51.36	51.36
Propane +	44.10	—	—	—	—	—	—	—	—	—
Nitrogen inerts	28.01	194.48	1,862.97	1,862.97	1,862.97	—	—	1,862.97	260.09	65.60
Oxygen	32.00	—	—	—	—	—	—	—	—	—
Water	18.02	—	—	410.99	—	410.99	—	—	—	—
Methanol	32.04	—	—	1,844.58	—	1,844.58	—	—	—	—
Ethanol	46.07	—	—	1,923.60	—	1,923.60	—	—	—	—
Propanols	60.10	—	—	425.50	—	425.40	—	—	—	—
Butanols	74.12	—	—	107.18	—	107.18	—	—	—	—
C_5 alcohols	88.15	—	—	44.57	—	44.57	—	—	—	—
Methyl acetate	74.12	—	—	52.68	—	52.68	—	—	—	—
Ethyl acetate	88.15	—	—	34.95	—	34.95	—	—	—	—
Total		3,049.24	86,405.10	67,860.66	61,563.51	6,297.15	2,930.40	58,633.11	7,991.43	5,136.39

Table 7.3 (Concluded)

Stream Flows (lb-mol/h)

	Molecular Weight	(19) Flash CO_2	(20) CO_2 Recycle From Synthesis	(21) Wet Alcohols	(22) Dried Alcohols	(23) Total Fuel to Reformer	(24) Air	(25) Flue Gases	(26) CO_2 from Separation I	(27) Steam From Reformer
Hydrogen	2.02	—	—	—	—	3,218.37	—	32.18	—	—
Carbon monoxide	28.01	—	—	—	—	23.69	—	34.31	—	—
Carbon dioxide	44.01	1,453.20	4,383.80	—	—	9.69	—	3,874.27	21,769.74	—
Methane	16.04	—	—	—	—	3,431.68	—	34.31	—	—
Ethane	30.07	—	—	—	—	99.35	—	1.00	—	—
Propane +	44.10	—	—	—	—	26.39	—	0.02	—	—
Nitrogen inerts	28.01	—	—	—	—	79.40	38,039.09	38,118.49	—	—
Oxygen	32.00	—	—	—	—	—	10,102.92	1,240.71	—	—
Water	18.02	—	—	410.99	10.58	—	—	10,384.59	—	55,441.67
Methanol	32.04	—	—	1,844.58	1,844.58	—	—	—	—	—
Ethanol	46.07	—	—	1,923.60	1,923.60	—	—	—	—	—
Propanols	60.10	—	—	425.40	425.40	—	—	—	—	—
Butanols	74.12	—	—	107.18	107.18	—	—	—	—	—
C_5 alcohols	88.15	—	—	44.57	44.57	—	—	—	—	—
Methyl acetate	74.12	—	—	52.68	52.68	—	—	—	—	—
Ethyl acetate	88.15	—	—	34.95	34.95	—	—	—	—	—
Total		1,453.20	4,383.80	4,843.95	4,443.62	6,888.77	48,142.01	53,519.88	21,769.74	55,441.67

Table 7.4

MIXED ALCOHOLS FROM NATURAL GAS USING THE DOW/UCC PROCESS: MAIN ENERGY FEATURES OF SRI'S DESIGN CONCEPT

Process Aspect	Main Quantitative Data			10^6 Btu/hr
Overall energy efficiency	Natural gas feed			3,346
	Natural gas fuel*			705
	Total (HHV basis)			4,051
	Mixed alcohols product			2,437
	Energy efficiency (HHV basis)			60.2%
Reformer furnace fuel	Natural gas fuel			690
	From purge (Stream 18)			1,110
	Total (HHV basis)			1,800
Distribution of reformer thermal input	Feed preheat and endotherm			1,330
	Steam generation system			150
	Air preheat			130
	Losses			180
	Total (HHV basis)			1,800
Energy for HP steam generation	Total required			1,730
	Source			
	Heat recovery from reformer and synthesis			1,570
	Reformer furnace			160
	Total			1,730
Steam utilization		lb/h	BHP	
	CO_2 compression	342,000	60,000	
	Makeup syngas compression	655,940†	34,000	
	Electricity generation	155,390	27,260#	
	Total	1,153,330		
Recovered thermal energy	Source:			
	Reforming			1,740
	Synthesis			600
	Total			2,340
	Utilization			
	CO_2 separation			140
	Steam generation			1,570
	Feed preheat			560
	Miscellaneous + losses			70
	Total			2,340

* Includes additional requirement for startup.

† Driven by noncondensing turbine, which exhausts at 440 psia to furnish reformer steam.

For the generation of 20 MWh/h of electricity.

Table 7.5

MIXED ALCOHOLS FROM NATURAL GAS USING THE DOW/UCC PROCESS: PRODUCT ENERGY CHARACTERISTICS

Component	HHV (Btu/lb)	LHV (Btu/lb)	Composition (wt%)
Methanol	10,259	8,588	30.77
Ethanol	13,321	11,535	46.12
Propanols	14,810	13,229	13.30
Butanols	15,792	14,227	4.14
C_5 alcohols	16,523	15,017	2.04
Methyl acetate	9,461	8,468	2.03
Ethyl acetate	11,185	10,114	1.60
Mixture	12,632	10,951	100.00

Specific gravity of mixture	0.797
Pounds per gallon	6.64
Blending octane value ([R+M]/2)	120*
HHV on volumetric basis (Btu/gal)	83,864
LHV on volumetric basis (Btu/gal)	72,715

* With regular unleaded gasoline base stock having (R+M)/2 of 85–87; blending octane value is lower than 120 with higher octane gasolines.

Table 7.6

MIXED ALCOHOL FROM NATURAL GAS USING THE DOW/UCC PROCESS: CAPITAL INVESTMENT

Plant Capacity: 16,600 b/sd or 5.45 million b/y (equivalent to ~690,000 mt/y) at a 0.90 stream factor
PEP Cost Index = 445; U.S. Gulf Coast Location

	Millions of Dollars
Battery limits	
Steam reforming (including steam generation)	104
Alcohols synthesis	48
CO_2 Separation–I	65
CO_2 Separation–II	37
CO_2 Separation–III	13
Product purification	9
CO recovery	5
Total battery limits	281
Offsites	
Tankage	45
Waste treatment facilities	52
General service facilities	79
Total offsites	176
Total Fixed Capital	457

Table 7.7

MIXED ALCOHOLS FROM NATURAL GAS USING THE DOW/UCC PROCESS: PRODUCTION COSTS

Plant Capacity: **16,800 b/sd or 5.45 million b/y (equivalent to ~690,000 mt/y) at a 0.90 stream factor**

PEP Cost Index = 445; U.S. Gulf Coast Location

	Millions of Dollars	
Capital Investment		
Battery limits	281	
Offsites	176	
Total fixed capital (TFC)	457	
	Cents per Pound	**Dollars per Barrel**
Production Costs		
Raw materials and utilities		
Natural gas, $N/10^6 Btu	2.07N	5.767N
Catalysts, miscellaneous	0.30	0.837
Maintenance materials, 1.5%/y of BL costs	0.28	0.773
Utilities	nil	nil
Variable cost	2.07N+0.58	5.767N+1.610
Labor		
Operating labor, 8 men/shift, $21.82/man-hour	0.10	0.280
Maintenance labor, 1.5%/y of BL cost	0.28	0.773
Control laboratory, 20% of operating labor	0.01	0.028
Total labor	0.39	1.081
Additional cash costs		
Plant overhead, 80% of total labor	0.31	0.865
Taxes and insurance, 2%/y of TFC	0.60	1.675
G&A, sales, research	0.36	1.000
Total cash cost	2.07N+2.24	5.767N+6.231
Capital related costs (CRC), 20%/y of TFC	6.01	16.754
Total cost (including CRC)	2.07N+8.25	5.767N+22.985

Figure 7.1

MIXED ALCOHOLS FROM NATURAL GAS USING THE DOW/UCC PROCESS:
SIMPLIFIED BLOCK DIAGRAM

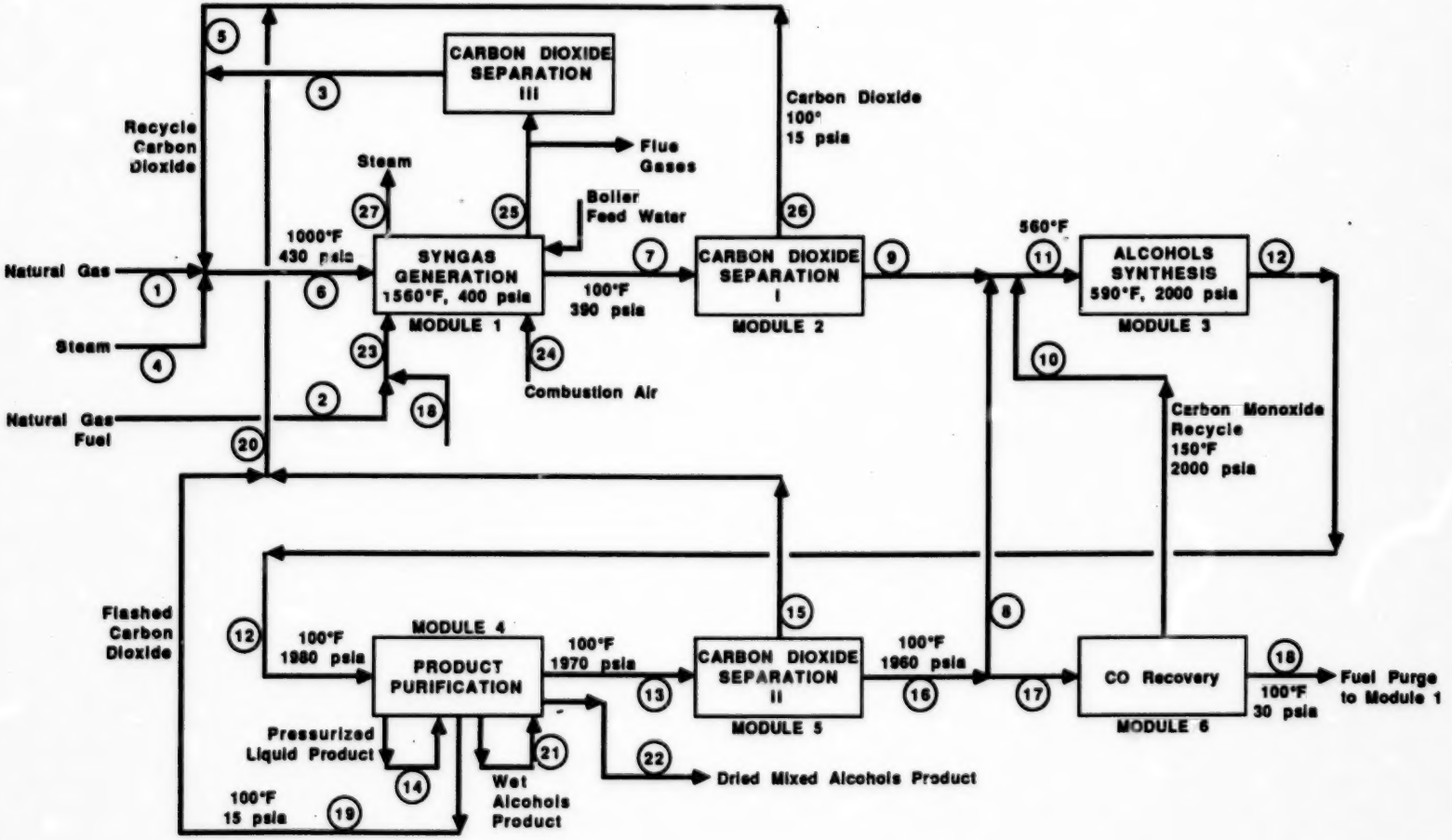
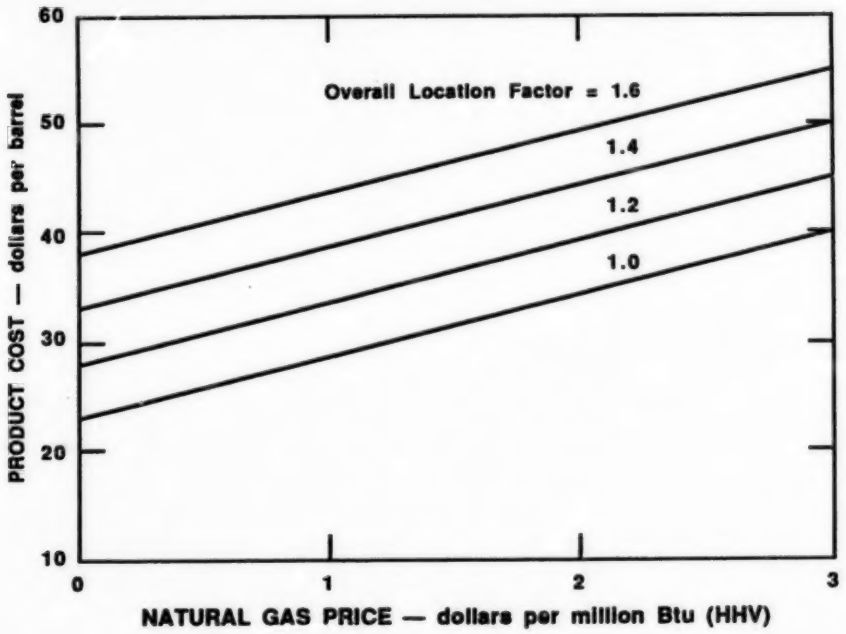


Figure 7.2

MIXED ALCOHOLS FROM NATURAL GAS USING THE DOW/UCC PROCESS:
Product Cost as a Function of Natural Gas Price and Location Factor



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